Relationships between floc properties and NOM removal using a moorland water source

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I, Margaret Balls confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.

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Abstract

Natural organic matter, or NOM presents a treatment challenge to the conventional water treatment process and has been associated with the formation of disinfection by-products (DBP's) such as Tri-halomethanes (THM's) if not removed prior to the disinfection stage. Poor removal of NOM is also thought to lead to filter performance problems such as turbidity or particle count breakthrough, which represents an increased risk of passage of *Cryptosporidium* into the treated water. Understanding the complex nature of NOM floc and how its physico-chemical properties relate to the coagulation matrix within the water treatment process is therefore key to optimising NOM removal. This forms the basis of the study which was carried out entirely using a natural raw moorland source water, which is preferable over synthetic kaolin based systems. The experimental programme encompassed both bench-scale and pilot-scale tests, and investigated the effect of changes to a number of variables such as coagulant type, coagulation pH and Fe:DOC ratio on floc physico-chemical properties. The approach taken in this work, of monitoring NOM removal alongside floc properties obtained from the optical flocculation monitor revealed some key trends. Firstly under equivalent shear conditions the coagulant dose almost always correlated with the steady-state maximum floc size, and influenced the flocculation rate. Generally the ferric based systems with the largest and fastest forming floc correlated with the best NOM removal, but when the applied Fe:DOC range was narrow and within an optimal range it was difficult to pin-point the best dose. The organic coagulants polyDADMAC and Zetag 64 formed larger, amd more reversible floc than the ferric based systems but with poor NOM removal. Secondly under equivalent shear conditions the larger flocs exhibited the least resistance to breakage, regardless of the coagulant system. Finally with regard to floc physico-chemical properties and filter performance, some key trends were revealed. Zeta potential influenced both NOM removal and the filtered water quality with considerable improvement noted as the charge tended towards 0 mV, and poor performance in the form of breakthrough as the charge decreased to <-10 mV or >4 mV. Flocculant dosing prior to filtration increased floc reformation and prevented breakthrough when charge destabilisation was sub-optimal, and could prove a useful strategy to employ when experiencing challenging winter conditions.

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Abbreviations

FI Flocculation index

FI_{max} Maximum flocculation index

FI_{break} Flocculation index directly after breakage period

FI_{ref} Flocculation index at the end of the modified jar test

R_{FI} Maximum rate of increase in flocculation index with time

F_{brk} Floc strength factor

F_{ref} Floc reformation factor

DAF Dissolved air flotation

NOM Natural Organic Matter

UV_{254} Ultraviolet Absorbance at wavelength 254nm

NTU Nephelometric Turbidity Units

ZP Zeta Potential

THM Tri-halo methane

TOC Total Organic Carbon

DOC Dissolved Organic Carbon

WTW Water treatment works

DI Deionised water

PDA Photometric Dispersion Analyser

GLI Great Lakes Instruments

AWWARF American Water Works Association Research Foundation

Da Daltons

DBP Disinfection By-Product

DI De-Ionised

DWI Drinking Water Inspectorate

DVLO Derjaguin Verwey Landau Overbeek

FA Fulvic Acid

FAF Fulvic Acid Fraction

HA Humic Acid

HAA Halo Acetic Acid

HAF Humic Acid Fraction

HPLC High Performance Liquid Chromatography

HPSEC High Performance Size Exclusion Chromatography

MIEX® Magnetic Ion Exchange Resin

MW Molecular Weight

NTU Nephelometric Turbidity Units

polyDADMAC Polydiallyldimethylammonium chloride

PSD Particle Size Distribution

RPM Revolutions Per Minute

SUVA Specific Ultraviolet Absorbance

THM Trihalomethane

THMFP Trihalomethane Formation Potential

Fe:DOC Ferric to DOC ratio (mg per mg)

ML/D Megalitres per Day

DEFRA Department of Environment Food and Rural Affairs

Meq/l Milliequivalents per litre

EPSRC Engineering and Physical Sciences Research Council

SSF Slow Sand Filters

RGF Rapid Gravity Filters

GC-MS Gas Chromatography Mass Spectroscopy

IWA International Water Association

Mv Millivolts

V Volts

Ma Amps

Notation

η_R Dimensionless deposition or removal rate of particles

η_T Dimensionless transport rate

α Attachment efficiency

Pe Peclet number

a_c the diameter of the spherical collector

U approach velocity

D_∞ diffusion coefficient at infinite separation

H Head loss after time t

C Filtrate concentration

C_0 Influent concentration

v approach velocity (volumetric flowrate per unit face area)

F Filterability number

Q_a airflow rate in cubic feet per minute per square foot

V_{mf} minimum fluidisation velocity

X mean

σ^2 variance

ε average energy dissipation

μ viscosity

ν kinematic viscosity

G average velocity gradient

λ Kolgomoroff microscale

p t-test probability factor

r^2 Coefficient of regression

Chapter 1 Introduction

Part 1.0 Project background

Natural organic matter or NOM is present in all surface water sources to some degree, with surface waters originating from upland sources containing high levels of NOM which can vary in concentration and treatability in a seasonal manner. NOM presents a risk to the drinking water treatment process as it is associated with the formation of harmful disinfection by-products such as Tri-halomethanes (THM's), and the passage of contaminants such as heavy metals, and pathogens such as *Cryptosporidium Parvum.* A well designed and operated drinking water treatment plant should be able to treat the incoming raw water containing NOM to minimise the above risks, but with regulatory standards becoming stricter there is an increased focus on improving the efficiency of existing treatment processes. The general treatment procedure for NOM removal in the UK is a multi-stage process involving the following stages:

1. Coagulation (charge destabilisation of the colloidal NOM by use of a coagulant such as ferric sulphate or Alum)
2. Flocculation (growth of primary particles generated from stage 1 into large floc)
3. Flotation or Sedimentation (solid-liquid separation of flocculated material by settlement or by flotation via upflow of saturated air in water)
4. Filtration (removal of flocculated material remaining from stage 3)
5. GAC adsorption to remove taste and odour compounds
6. Disinfection (destruction of pathogens using a disinfectant such as chlorine)

The fundamental purpose of the upland surface water treatment process is to facilitate the removal of NOM during stages 1-4, so that disinfection can be concentrated on its primary purpose which is destruction of pathogens without the risk of producing tri-halo methanes (THM's) and other disinfection by-products. In order to optimise the NOM removal process as described in stages 1-4, it is crucial to have a good understanding of the physico-chemical properties of the floc formed in stages 1 to 2 and how these can be affected throughout the treatment process, and ultimately impact on the final solid-liquid separation stage of filtration.

Part 1.1 Motivation for research

Yorkshire Water has many flotation treatment plants that abstract water from the moorland surface water catchment, and on several of these plants they experience treatment problems in the cold winter months. One of these treatment plants, Albert WTW in Halifax has been studied during this research work. This problem can be characterised by premature filtered turbidity breakthrough which is shown below in figure 1. The filtered turbidity breakthrough starts at 0.4 m headloss which is well below the terminal headloss which the filter should initiate a backwash (2m). Figure 1 shows that during December 2002, the period of acceptable filtered water quality was less than 12 hours, and breakthrough started very early in the filter run on some days. This type of filter performance increases the risk of a *Cryptosporidium* failure, and if not properly managed can lead to a cycle of poor filter performance and poor filter operation. The latter is caused by the increased frequency of filter washing which imparts flow changes on the remaining "in service" filters. This can increase the severity of the breakthrough from the "in service" filters depending what stage the filters were at during the filter run when they were subjected to a flow change. The exact reasons for the filter breakthrough and suitable solutions are not known, and form the basis for this research project.

Prevention of filtered turbidity breakthrough is of importance when optimising the overall NOM removal process, as the filtration process is the final barrier between the upstream processes and disinfection. In order to understand the reasons for the filtered turbidity breakthrough and find process solutions, it is important to understand the nature of the floc formed during the upstream treatment process as floc formation and removal is fundamentally at the heart of the NOM removal process. The exact reasons for the shortened filter run times and filtered turbidity breakthrough shown in figure 1 aren't known; but there is a growing body of evidence that suggests that NOM floc structural properties can change significantly dependant on the ratio of the coagulant dose to the NOM content (Jarvis *et al.,* 2004). This change in structure could influence floc properties that relate to treatment performance, and in particular filter performance. It is also known that the floc passing through the flotation units at Albert WTW is considerably fragmented by the impact of the shear forces as it passes through the stream of air bubbles (Zhang *et al.,* 2009). This may impact on the filtered turbidity breakthrough typically experienced in the cold winter months.

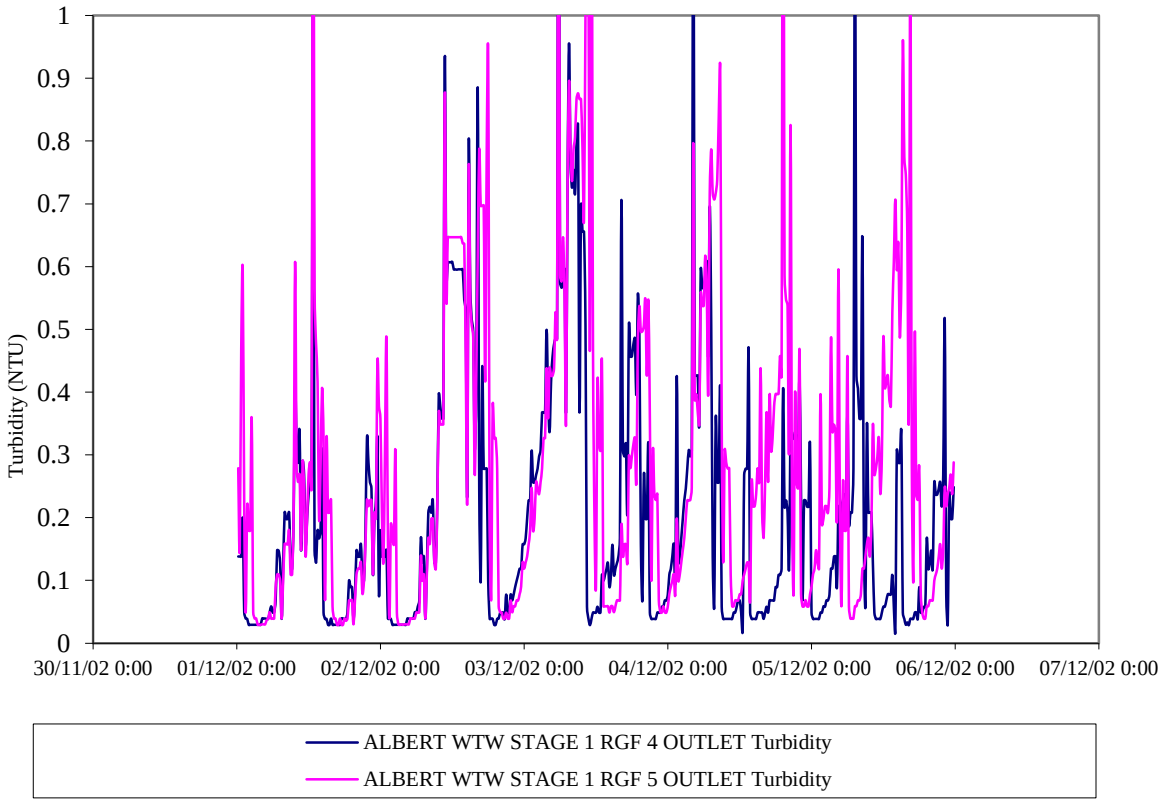

Figure 1 Filtered turbidity breakthrough on rapid gravity filters 4 and 5 at Albert WTW, December 2002, 6°C

Operationally important floc physico-chemical properties include surface charge, size and strength and their influences are summarised in table 1. The literature referred to in table 1 indicates that floc properties such as size, strength and charge can all be related to coagulant dose relative to the NOM concentration. The aforementioned floc properties are thought to be important with regard to the NOM removal process as a whole; but the relative importance of charge, size and strength aren't known.

Floc Property	Importance relative to NOM removal via coagulation	Importance relative to filter performance
Size	Impact of NOM on sludge floc with and without humic acid showed presence of humic acid reduced floc size (Dulin and Knocke, 1989) Increased DOC:Fe lead to significant impact on floc structure; reduced floc size, settling rate, strength and degree of compaction (Jarvis *et al.*, 2004)	Smaller particles have a lower rate of capture during filtration mechanisms (Cleasby, 1999) It is known that the smaller particles in the size range 1-10µm are the most challenging to remove in depth filters (Kim and Tobiason, 2004; O'Melia, 1985; Jegatheesan and Vigneswaran, 2005)
Zeta potential	An optimum band of +2 to + 4 mV reported for alum coagulation at pH 6.0 and -4 to + 4 mV at pH 7.4 (Gregory and Carlson, 2003) Sharp *et al.* (2004) reported an optimal range for good DOC removal of -10mV to +3 mV	Attachment processes are thought to be retarded if zeta potential isn't optimal (McCarthy and Zachara, 1989) Lower bound of zeta potential reported for filter performance to be -10 mV (Logsdon *et al*., 2002)
Strength	Reduction in floc strength noted with high NOM loadings (Jarvis *et al*., 2005)	Floc size and strength reported to be intricately related to filter performance. Higher Camp numbers formed smaller weaker floc with lower headloss development rate in direct filtration (Bache and Gregory, 2007)

Table 1 Floc properties and their linkage with NOM removal and filtration processes

Part 1.2 Scope of work

The main scope of this research was to use an optical flocculation technique to study floc physico-chemical properties of floc formed from using Albert WTW raw water, and to directly compare with NOM removal performance parameters. Some of the work was carried out at UCL laboratories, but the majority was carried out at Albert WTW and at all times the raw water used originated from Albert WTW catchment. At the time that this research was carried out, there were not many studies involving real natural waters and laboratory based floc strength techniques.

Since this research was carried out, there has been an increase in these types of studies but the predominant method used by researchers has been to use synthetic or model waters rather than natural raw waters. This research is the first to have studied the relationship between the floc properties of floc strength and floc reformation as measured by a photometric dispersion analyser (PDA) alongside zeta potential, NOM removal and filter performance using a natural raw water. The use of the optical flocculation monitoring technique using a PDA to study re-flocculation of plant treated water prior to filtration is also the first of its kind. There are other techniques available that can be used to measure floc strength and reformation, such as the Mastersizer 2000. The Mastersizer 2000 has the benefit of quantifying the floc size which the PDA doesn't, but the drawback of the Mastersizer 2000 is the size of the equipment which makes it less mobile. The PDA is small, portable and easy to use and could potentially be operated by plant technicians with relatively little training. This was the main reasoning for using the PDA over the Mastersizer 2000.

Part 1.3 Concurrent Research at Yorkshire Water

This project was devised to address a real issue experienced at a Yorkshire Water treatment plant in Halifax. The research was tailored towards understanding a complex system involving a natural moorland water, with the majority of the research carried out onsite at Albert WTW and at all times using Albert WTW raw water. The characteristics of the raw water were changeable and this has been taken into account within the discussion of results. At the time of this research, a project was carried out by Sharp (2005) which involved evaluating the nature of NOM within the raw water at Albert WTW. Some of the conclusions from Sharp (2005) have been used to explain some of the results generated from this work, and it is clear when this has been done. Albert WTW has also been the subject of a number of other characterisation and optimisation studies (Goslan, 2003; Fearing, 2004, Jarvis, 2004) around a similar time-frame to this research, and outputs from their work have also been taken into account where relevant.

Part 1.4 Project aims and objectives

The main aim of this thesis was to investigate the use of an optical flocculation monitoring technique to determine floc properties, in order to investigate correlations that may exist between floc properties and the NOM removal process for a natural water source. In order to achieve this, particular emphasis was placed on the following:

1. The impact of changing coagulant type and dose on NOM removal and floc properties.
2. The effects of changing coagulation pH and Fe:DOC ratio on floc properties and NOM removal.
3. Changing Fe:DOC ratio and the impact on floc properties, NOM removal and filtered water quality.
4. The use of polyelectrolytes to alter floc properties upstream of filtration, and the impacts on filtered water quality.

In order to fulfil the overall project aim, the experimental work plan focused on the following within the results chapters:

1. Chapter 4 - Jar tests and breakage jar tests using the PDA and different coagulants and combinations of coagulants to determine impact of coagulant system on floc properties and NOM removal.
2. Chapter 5 - Jar tests and breakage jar tests to determine impact of Fe:DOC ratio and coagulation pH on floc properties and NOM removal.
3. Chapter 6 - Pilot plant trials using the DA20 pilot plant and pilot filter to examine inter-relationships between Fe:DOC ratio, floc properties, NOM removal and filter performance.
4. Chapter 7 - Jar tests and breakage jar tests using Albert WTW pre-filtered water and polyelectrolytes to determine effect of dose/polyelectrolyte type on floc properties.
5. Chapter 7 - Pilot filter trials using Albert WTW flotation outlet water and polyelectrolytes to determine the effect of dose/polyelectrolyte type on floc properties and filter performance during winter conditions that are usually associated with the poor filter performance depicted in figure 1.

Part 1.5 Thesis Structure

The overall background to this research project, and its overall aim and objectives have been defined in this chapter. A review of relevant literature is provided in Chapter 2. The experimental methodology and detail of the pilot plant design and operating procedure can be found in Chapter 3 and appendix 1. The main bulk of the results and discussions can be found within Chapters 4 to 7; each individual chapter has a conclusions section at the end. Chapter 8 provides an overall discussion which details the main experimental findings and their relation to previous work, and how the field of study has been furthered by this project. Chapter 9 contains the conclusions from the project in relation to the overall aim as described in this chapter, and the recommendations for further work. This project was presented in the form of an oral presentation and poster presentation at the EURESCO conference in Acquafredda di Maratea, Naples, Italy, 2003. The work was also presented at the 8th IWA particle separation conference, Seoul, Korea, 2005, and published in *Water Science and Technology*, volume 53, no 7 (included in Appendix 4).

Chapter 2 Literature Review

Part 2.0 What is Natural Organic Matter?

Natural organic substances are present in varying concentrations in all natural surface waters. These organic substances are generally referred to as natural organic matter or NOM as it is usually abbreviated. The dominant fraction of aquatic NOM is comprised of humic substances. Humic substances have the chemical properties typical of weak anionic polyelectrolytes; they have molecular weights of several hundred or larger (Visser, 1985) and carry weakly acidic functional groups such as carboxylic and phenolic groups (Cook and Langford, 1998). Humic substances can be defined as a general category of naturally occurring biogenic, heterogeneous organic substances that can generally be described as being yellow to black in colour, of high molecular weight, and refractory products of decomposition or primary plant material by microbes (Schnitzer and Kahn, 1972). Modern techniques such as differential spectroscopy have allowed researchers to formulate a clearer picture of what the structure of humic molecules look like but this is still subject to large regional and seasonal variation, as is the reactivity and treatability of these molecules.

The properties of NOM vary from system to system in poorly understood manners depending on the origin and history of the water sample. The origin of aquatic NOM is mainly from decaying vegetation. NOM consists mainly of humic and fulvic acids, otherwise known as humic acids. Humic acid can be defined as the fraction of humic substances that is not soluble in water under low pH, but is soluble at high pH. Fulvic acid can be defined as the fraction of humic substances that is soluble in water under all pH conditions. Humic acids have a higher molecular weight than fulvic acids. The lower molecular weight fulvic acids have a higher oxygen content but lower carbon contents than the higher molecular weight humic acids. Fulvic acids contain more functional groups of an acidic nature, particularly carboxylic acid groups. Humic substances consist of a heterogeneous mixture of compounds for which no single structural formula will suffice, and it is for this reason that their removal is complicated. Humic acids are thought to be complex aromatic molecules with amino acids, amino sugars, peptides and aliphatic compounds. Fulvic acid is thought to contain both aromatic and aliphatic structures, both extensively

substituted with oxygen containing functional groups. Another humic substance is humin which is insoluble in both dilute acid and dilute base, and its importance in understanding the role of aquatic NOM is therefore less important than fulvic and humic acids. Humins have the same characteristics as humic acids but there solubility in bases is hindered by the fact that they are associated with clay minerals in natural waters (Packham, 1964). It appears that the fulvic acid fraction is the most predominant group of humic substances in natural waters. The chemical structures of both humic and fulvic acids are not precisely known but the nature of the major functional groups is fairly well defined. The following types of functional groups have been reported (Schnitzer and Kahn, 1972):

- Carboxyl
- Phenolic
- Alcohol
- Methoxyl
- Carbonyl
- Ether
- Ester

Part 2.1 Why Remove NOM?

The removal of NOM from drinking water has been deemed of great importance for the following reasons:

- Humic substances are especially reactive with a variety of oxidants and disinfectants that are in widespread use in water treatment plants, particularly chlorine. The products of this reaction are known as disinfection by-products and include substances such as tri-halo methanes, haloacetic acids, and a host of other halogenated by-products, a number of which have been shown to cause cancers in laboratory animals. The most sustainable method of reducing disinfection by-products is to remove the precursors and optimise the primary treatment upstream of disinfection (Singer, 1999).
- Humic substances give the water an unsightly brown colour and odour which is unacceptable to the customer.
- The presence of NOM in the distribution system can lead to microbial re-growth and the formation of bio-films.

- Adsorption interactions of NOM with particles in aquatic environments have been linked with the transport of micropollutants through the water treatment process.

It has been shown in a study of disinfection by-product (DBP) formation using hydrophobic organic material extracted from natural waters using an ionic exchange resin called XAD-8 that THM and halo-acetic acid (HAA) formation was directly proportional to the total organic carbon (TOC) concentration in synthetic solutions prepared from different hydrophobic extracts (Singer et al., 1999). These results were confirmed by studies utilizing different techniques for extracting and fractionating NOM. These techniques are discussed at a later stage and the findings from the aforementioned study by Singer (1999) clearly identify NOM as a route for the formation of DBP in the drinking water treatment process. Removal of NOM from the raw water is therefore a key driver in optimising drinking water treatment performance in areas where NOM is prevalent as compared to turbidity and suspended solids.

Part 2.2 Techniques for Analysing and Characterising Aquatic NOM

The character of the NOM is dependent both on the source from which it is derived and the chemical and biological degradation to which it has been subjected (Bruchet et al., 1990). There are four main techniques used for the analysis of NOM:

1. Analysis of the dissolved organic carbon (DOC) is one method of quantifying the NOM in a raw water sample. Dissolved organic carbon in waters includes humic substances as well as smaller molecular weight proteins, carbohydrates and amino acids (Collins et al., 1985; Thurman and Malcolm, 1981). The method involves filtering the sample through a 0.45µm membrane and then injecting the sample into a total organic carbon analyser. This gives a reading of the DOC in mg/l.
2. UV spectrophotometry is a commonly used method in industry, as the instruments are not expensive and are easy to maintain. This method involves filtering the water sample through a 0.45µm membrane filter and measuring the absorbance of the filtrate using a UV spectrophotometer. The reading obtained from the spectrophotometer gives an absorbance reading per unit area of the spectrophotometer cell. The UV-to-DOC ratio can provide an indication of the degree of unsaturated C-C bonds of the NOM in the source

water and a higher UV absorbance-to-DOC ratio can be indicative of greater complexity resulting from increased aromaticity and of other unsaturated chemical bonds (Goel *et al*., 1995). The higher molecular weight substances such as humic acid are characterised by having a UV_{254}absorbance/DOC ratio of 0.03-0.05. The lower molecular weight compounds such as fulvic acid have a UV_{254}absorbance/DOC ratio of 0.02 (Tambo and Kamei, 1998). Some waters with a dominance of lower molecular weight NOM are difficult to treat by coagulation (Krasner and Amy, 1995). In some studies it has been found that there is preferential removal of NOM that absorbs ultraviolet light indicating a preferential removal of aromatic NOM (Krasner and Amy, 1995). In water treatment practice, the use of absorbance at a wavelength of 254nm has been found to be useful for monitoring the concentration of DOC (Owen *et al.*, 1995). This is a very practical technique as it can be carried out onsite by trained plant operators and the result is available instantly, rather than DOC which is usually carried out in a laboratory.

3. High performance size exclusion chromatography (HPSEC) separates organic compounds by molecular size through a permeation medium process. In this process the organics pass through a medium containing many small pores. The larger compounds have less retention time in the pores compared with smaller compounds. The organic compounds are selectively eluted from the column according to size with the larger molecular size eluting first. The elution time is converted to an apparent molecular weight using polystyrene sulphonate standards. Extensive work has been carried out on the characterisation of NOM and the effect of its character on treatment capability. This work found that the NOM fractions change in proportion throughout the seasons, with the fulvic acid fraction (FAF) showing the greatest increase during autumn and winter, and the charge density of this fraction also increased. The DOC was found to be stable despite the change in NOM proportions (Sharp *et al*., 2004). This has implications on the ability of the coagulant used at the water treatment plant to cope with the changing nature of the incoming raw water NOM as the coagulant demand is tailored to the hydrophobic component of the NOM. The hydrophilic component remaining is thought to give rise to significant quantity of disinfection by-products where chlorine is the disinfectant (Sharp *et al.,* 2006) so it can be seen that optimising removal of NOM is of importance.

4. Diffuse reflectance Fourier transform infrared spectroscopy (DRIFT) can be used to identify the functional groups in the sample and was studied by Capriel *et al*. (1997) who found that:

    - DRIFT can provide information on the major functional groups found in NOM
    - Comparison of the DRIFT spectra of raw and coagulated waters can provide information on the functional groups present before and after coagulation and therefore which groups are problematic to remove.
    - Inorganic salts can interfere with the results, and knowledge of the constituent salts is required before the spectra can be interpreted

In order to understand how to optimise existing systems for NOM removal a more detailed knowledge of the structure and reactivity of humic substances is required. Humic substances are known to contain several well-known functional groups such as carboxylic acids and alcohols. By utilising this fact, researchers have been able to adapt existing chemical analysis technologies to learn more about the structure of humic substances and how they behave in the aquatic environment. Typical parameters that can be measured using existing technology are dissolved organic carbon (DOC), spectral parameters such as UV/VIS/IR absorbance, high performance size exclusion chromatography (HPSEC), and elementary analysis. Measurement of the DOC allows the quantification of the organic carbon content in mg/l. Spectral analysis of UV/VIS/IR absorbance can be used to provide information about structure and functionality (Grasso et al., 1989). Several research projects have focused upon isolation and fractionation of refractory organic substances (ROS) by membrane filtration or gel chromatography and determination of each fraction using sum parameters (Leenheer *et al* 1999; Abbt-Braun *et al*., 1991; Perdue, 1989). They found that only a rough pattern of the DOC fractions was achieved, and denaturation of the organic material couldn't be avoided. A combination of gel chromatography with continuous detection of DOC, UV absorbance and dissolved nitrogen has been found to be a very useful analytical tool for characterising humic substances (Huber and Frimmel, 1996).

The technique of differential spectroscopy is also a useful tool for monitoring transformations in the chemical state of humic species as it can be used to identify the DBP forming potential of the substance. The absorbance of light by humic substances is a very important parameter than can be measured in-situ relatively easily and inexpensively using a spectrophotometer. The absorbance of light by humic substances is an additive quantity of all light absorbing groups in the substance plus an additional contribution from inter-chromophore interactions (Korshin *et al*., 1999). The measurement of UV at wavelength 254 nm is most widely used to monitor humic substances. Light absorption by humic substances at $\lambda > 250$nm is largely attributable to aromatic chromophores in the molecules (Traina *et al*.,1990; Novak *et al*., 1992). The differential absorbance can be defined as the change in absorbance of the sample (initial minus final) in response to any forcing function.

This contrasts to conventional spectroscopy which focuses on analysis of all the chromophores in a sample, whereas differential spectroscopy focuses on the behaviour of those chromophores affected by the forcing parameter. This technique is very useful when assessing the effect of parameters such as pH and more importantly, the reaction of the humic species with oxidants such as chlorine. It has been found that there is a very strong correlation between the accumulation of disinfection by-products and the magnitude of differential absorbance (Korshin *et al*., 1999). The removal of NOM by conventional water treatment utilising inorganic coagulants (discussed in part 2.6) is affected by the NOM humic acid/non humic acid fractions, the hydrophobicity/hydrophilicity character and molecular weights of its constituents (Krasner and Amy, 1995, Owen *et al*., 1995). Important work has been carried out to assess the importance of the character of the NOM on its removal potential using conventional coagulants such as alum. A comprehensive study using different raw waters was carried out by Chow *et al*. (1999) using five techniques for the characterization of the NOM. This provided useful insights into the compounds of NOM that remain recalcitrant to removal by alum addition. The five techniques used were pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS), diffuse reflectance Fourier transform infrared spectroscopy (DRIFT), high performance size exclusion chromatography (HPSEC), UV absorbance (UVA) and dissolved organic carbon analysis (DOC). They found that the compounds that remained recalcitrant to alum addition were potentially formed from biopolymer compounds. Improved removal of these compounds could

be facilitated by overdoses of alum. The main problem in extrapolating results from studies like the one illustrated is that the character of NOM is dependent on the source and season, and studies involving raw waters are therefore difficult to interpret and relate to other studies involving raw waters of different origin. However it is useful to see that the different analysis techniques used gave consistent results.

Part 2.3 Overview of NOM Removal Technologies

There are four main commercially viable technologies for the first-stage removal of NOM within the drinking water treatment process, and these are:

1. Coagulation/Flocculation - Humic acid in solution is a weakly anionic polyelectrolyte and can therefore react with suitable cations to form insoluble precipitates. There are many cationic reagents in use but the most common are hydrolysing metal salts such as aluminium sulphate and ferric sulphate. Recently the use of coagulants comprised of inorganic and organic components has been studied. Composite inorganic-organic coagulants such as poly ferric chloride and poly DADMAC were investigated by Wang *et al*. (2008) and found to perform well with respect to removal of NOM. The cationic reagent or coagulant should ideally neutralise the negative charge carried on the functional groups of the NOM molecule and then facilitate formation of a primary particle and then floc which can be removed by solid/liquid separation techniques. Flocculation is the name given to the stage occurring immediately after coagulation where particle aggregation of the coagulated NOM occurs and large visible flocs are produced. This is mentioned in greater detail in part 2.4. The resulting flocs can then be settled and removed or floted and removed. It is recognized that optimisation of these two stages will increase the overall efficiency of the water treatment plant. Any floc that remains suspended in the water after the separation stage is removed in filters on a conventional treatment plant. Coagulation using hydrolysing metal salts is the most common method of treating surface water containing NOM, for it is considered the most economical and efficient method, and most water plants in the U.K are based upon this technology.

2. Membrane Filtration - Membrane or nano-filtration was first researched in Norway in 1975 (Odegaard and Kootatep, 1982) and the first full-scale plant was put into operation in 1990 and up to 100 have been commissioned to date in Norway (Odegaard *et al*., 2010) . It is relatively uncommon in the UK. Humic substances being large in size (1000- 100,000 Da) can be separated from water by physical means such as molecular sieving through membrane filters. The typical pore size used in these membranes which can be made from cellulose acetate or polyamide is 1000-2000 Da and they are operated at 4-8 bar (Odegaard *et al*., 2000). Membrane processes are used for desalting, softening, dissolved organics, colour removal, and particle removal. Membrane processes are classified by the driving force used to promote the water treatment:

    - Pressure
    - Electrical Voltage
    - Temperature
    - Concentration Gradient
    - Combination of more than one driving force

    Coloured surface water contains organic substances with a broad range of molecular sizes and weights (Owen *et al*.,1993). The size of the membrane pore is therefore of prime importance. The smaller the pore size, the greater the removal of impurities but the higher the pressure required; and therefore a higher operating cost. Also, the smaller the pore size the greater the chance of removal of inorganic ions. Of these, di and tri-valent cations are known to coagulate humic substances. Increased concentrations of both humic substances and these ions will arise on the membrane surface and promote membrane fouling and declining membrane permeability (Thorsen, 1999). The wide range of molecular sizes present in NOM makes the choice of optimum membrane pore size dependant on raw water concentration and stability, and to some extent turbidity. This factor presents significant practical problems as it is highly probable that the raw water NOM concentration and character change with the seasons, and turbidity is not guaranteed to be low enough to not cause fouling.

3. Ion Exchange - Adsorption/Ion exchange as a method of removing NOM has recently been developed using different media and exchange resins. The following types of porous media are used in drinking water treatment systems:

    - Activated carbon
    - Anion exchange resins
    - Carbonaceous resins
    - Metal oxides

    Humic substances can be bound by all of these media to a certain extent, thus sorption processes are generally suited to NOM removal. Research by (Hwang *et al*., 1999, Croue *et al*., 1999) has shown that the most hydrophilic fractions of NOM which have been shown to be less amenable to removal by conventional methods are stronger DBP forming precursors than the corresponding hydrophobic NOM fraction. Activated carbon has been found to be effective in removing DOC, researchers have found that anion exchange resins give better removal of DOC (Afcharian *et al*., 1997). The efficiency of the anionic exchange resin depends on the origin and nature of the raw water. For larger NOM structures, the size of the pores and the molecular size distribution are important factors to be considered, for intermediate molecules the hydrophilic character of the resin matrix is important, while the exchange capacity is predominant for the low molecular weight NOM structures (Fu *et al*., 1990). Croue *et al*. (1999) found that the retention phenomena of NOM onto anion exchange resin is complex and integrates several mechanisms. More recently ion-exchange processes using MIEX^{R} have been found to reduce the coagulant demand on a moorland surface water treatment plant by removing a proportion of the NOM and reducing DOC at the works inlet (Fearing *et al*., 2004). There is a draw-back with using MIEX^{R} however, and that is the relatively high molecular weight hydrophobic component is known to foul the membranes and reduce the operating efficiency (Mergen *et al*., 2008).

4. Oxidation/Biofiltration - Oxidising agents such as chlorine, chloramine, chlorine dioxide and ozone have the potential to cause significant changes to the nature of humic substances. Ozone and ozone radical species have superior oxidizing abilities and break down rapidly. The reactions of humic substances with ozone have been quite comprehensively researched and the reaction by-products and mechanisms are thought to be well understood (Odegaard *et al*., 2010). Ozone reacts with humic substances (and other material) either through direct reactions involving molecular ozone or indirect reactions involving radical oxidation species produced from ozone degradation. Both types of reaction occur during typical water treatment and the extent of each type depends upon the conditions and the nature of the water quality. Ozonation causes substantial structural changes to the humic substances which include; a strong and rapid decrease in colour and UV-absorbance due to a loss of aromaticity and depolymerisation Camel and Bermond (1998); a small reduction in TOC; a slight decrease in the high apparent molecular weight fractions, and a slight increase in the smaller fractions; a significant increase of the carboxylic functions; and the formation of ozonation by-products (Langlais *et al*., 1991). These by-products have been reported to be mainly aldehydes (formaldehyde, acetaldehyde, glyoxal, methylglyoxal) and carboxylic acids (formic, acetic, glyoxylic, pyruvic and ketomalonic acids) Camel and Bermond (1998); glyoxalic acid and hydrogen peroxide have been identified as fulvic acid by-products (Xiang *et al*., 1992).

Results so far to date indicate that the ozonation of humic substances tends to increase their biodegradability, which is why the ozonation process is typically followed by bio-filtration (Odegaard *et al*., 2010). The earliest form of biofiltration was the slow sand filter, this method has been extensively reviewed by Lambert and Graham, (1995a). Slow sand filters give a removal of DOC between 5 and 40%. Where humic substances are the principal component of the DOC in the raw water, removal efficiencies of 9 to 15% have been achieved.

Part 2.4 Brief History of Coagulation Theory

The modern use of coagulants as water treatment aids started approximately 100 years ago, when ferric chloride and aluminium sulphate were used in full-scale drinking water treatment plants. Scientific-based study on coagulation/flocculation also started then, when the Schultz-Hardy rule was proposed to explain coagulation. The Schultz-Hardy rule states that ions having the opposite charge of a colloid particle are the most effective in coagulating the particle, and further, that increased ionic charge results in increased coagulating abilities. In 1917 Smolokowski developed the theory of particle collision function, which explains the change in particle number during the flocculation process. Mattson (1975) first deduced that the hydrolysis products of aluminium and iron were more important than the trivalent ions themselves. Black *et al.* (1934) conducted a series of studies on the effect of pH and various anions on the time of floc formation. For the next few years, efforts were concentrated upon the study of mechanical methods to produce better flocs and search for better coagulant aids. During this time, no new theories on coagulation were proposed.

In the late 1940's, a new coagulation theory was developed by Langelier and Ludwig, who distinguished two mechanisms for the removal of colloidal impurities (a) the double layer compression, a process to allow the particles to overcome the repulsive forces and thus agglomerate and precipitate; and (b) precipitate enmeshment, a process in which small particles are physically enmeshed by metal precipitates when they are forming and settling. These two mechanisms have been elaborated upon and substantiated on a theoretic basis by La Mar Healey (1963), who proposed the terms coagulation based on (a) and flocculation based on (b). A significant step in the development of comprehensive theory on coagulation was proposed by Black and Willems (1961) who introduced the concept of micro-electrophoresis to the study of colloid destabilization which allowed the quantification of electrical charge on colloidal particles. Study of the stoichiometric relationship between the coagulant dose required to neutralize the colloids and the concentration of colloidal impurities in the water also started in the 1960's. These studies highlighted the effect that pH, ionic strength, and the properties of the impurities to be removed have on the charge of colloidal particles. These studies also re-emphasised the importance of hydrolysis products, as originally proposed by Mattson (1928), and established an adsorption model to detail the mechanism of hydrolysed metal coagulants.

Study of the coagulation mechanism has always been linked to the need to meet increasing water quality standards. This was highlighted in the 1970's, when haloforms and halogenated organics such as trihalomethanes (THM's) were first found in treated waters (Rook, 1974), which result from the disinfection stage of the treatment process due to reaction of the disinfectant (chlorine) and natural organic matter. Since the 1980's, optimisation of the coagulation performance for the removal of NOM has been systematically studied (AWWA Research Committee Report, 1989) , using various real surface waters, by evaluation of a range of variables such as mechanical conditions for coagulation/flocculation , sequences of chemical addition, coagulant type and dosage, coagulation pH, restabilisation zones and water quality characteristics including water temperature. Another tool added to the coagulation technology was the streaming current detector (SCD) by Dentel and Kingery (1989), which is used alongside jar tests to determine the correct coagulation dosage. More about the streaming current detector is detailed in part 2.7.

In the 1990's, NOM and other precursors of disinfection by-products were still the main impurities causing concern. Coagulation/flocculation is affected by upstream treatment e.g. pre-oxidation process and in turn affects downstream treatment processes such as settling/floatation, filtration, activated carbon adsorption, oxidation and disinfection. During this decade, the effect of pre-ozonation on the coagulation performance, the coagulation treatability of various raw waters and different fractions of NOM, and the impact of coagulation performance on the effectiveness of carbon adsorption have been and still are being studied. In addition enhanced coagulation, either by increasing coagulant dose and lowering coagulation pH (e.g. Cheng *et al* 1995 and Crozes *et al* 1995), or through developments in coagulation chemistry to prepare more effective coagulants (Jiang and Graham, 1996) have been evaluated for improving the removal of NOM and general coagulation performance.

Part 2.5 Justification of Coagulation/Flocculation as a Method for NOM Removal

In order to justify the use of coagulation/flocculation as a method for the removal of NOM, the process must be shown to be:

- Efficient in achieving desired removal
- Cost effective in achieving desired removal
- Able to improve efficiency of removal as removal standards are increased

In comparison with other techniques that are available. In terms of removal efficiency, coagulation/flocculation has been shown to be effective but because the mechanisms behind the process are poorly understood with waters of changeable character, the technique is not as effective as it should be. This implies the process can be improved to increase the removal efficiency with greater knowledge of the treatability of NOM fractions. In comparison with membrane processes, coagulation/flocculation has considerably lower operating costs as it does not require the use of high pressure or expensive membrane modules. Also membrane processes are notorious for fouling when used in the application of NOM removal as discussed in part 2.3 . Unlike oxidation/biofiltration, it does not require the use, and storage of hazardous chemicals, such as ozone and chlorine, and with continued research, the amount of chemicals required for coagulation/flocculation may be decreased as the process is optimised. Adsorption/ion exchange processes are still in their infancy and removal efficiency is very dependent on the sorbent media used and hard to predict, partially because of the complicated interactions of the different fractions of NOM with the media. MIEX^{R} is a relatively new media that has in the past five years seen an increasing amount of usage as an initial treatment stage on the influent raw water. One of the main benefits appears to be increased removal of the difficult hydrophilic components, in some cases up to 60% (Mergen *et al*., 2008). There is still a need, even with MIEX^{R} to have coagulation/flocculation as a stage in the treatment process.

Part 2.6 The use of Hydrolysing Metal Salts as Coagulants

Coagulation is a process whereby small particles are combined with a coagulating agent to form larger particles (aggregates called flocs), dissolved organic matter can then adsorb onto these aggregates and be removed in further solid/liquid separation processes. Iron and aluminium salts are frequently used in industry as coagulants. When iron and aluminium salts are dosed into water, various hydrolysis products are formed rapidly and in an uncontrolled fashion (Tang and Stumm, 1987). Baes and Mesmer (1976) detailed the products formed when aluminium hydrolyses, namely Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^{+}$, $Al(OH)_3$ molecules, three polymeric species $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$ and $Al_{13}O_4(OH)_{24}$ and a solid precipitate $Al(OH)_3$. When iron hydrolyses the following products are formed, namely the five monomers Fe^{3+}, $Fe(OH)^{2+}$, $Fe(OH)_2^{+}$, $Fe(OH)_3$ and $Fe(OH)_4^{-}$, a dimer $Fe_2(OH)_2^{4+}$ and a trimer $Fe_3(OH)_4^{5+}$, and a solid precipitate $Fe(OH)_4^{5+}$ according to Flynn (1984). Additional dissolved polymeric Ferric species exist and these may be represented by the general formula $Fe_x(OH)_y^{(3x-y)}$ or $[\ Fe_xO_y(OH)_{x+r}]^{(2x-2y-r)+}$. These are kinetically stable and their thermodynamic equilibrium state depends on the conditions of preparation.

Conventionally, the appropriate dose of coagulant is determined experimentally by using the jar test method. Varying doses of coagulant are added to the raw water and the optimum dose is determined by evaluating the dose that gives the best removal of organic matter (usually measured by difference in UV_{254} absorbance between the raw water and dosed water) under specific conditions of temperature and pH and shear rate. Usually in the normal pH range of raw water of between pH 6-8, hydrolysis is rapid and uncontrolled according to Jiang (2001). The major drawback with the use of aluminium and ferric salts is the inability to control the nature of the coagulant species formed, and it is not known exactly how these reactions are effected by perturbations in temperature and pH. According to Jiang (2001) it is possible that the hydrolysis products adsorb to the colloidal surfaces to neutralise the charge or may interact chemically with dissolved components in the water. In order to counterbalance these drawbacks, it is usual for water treatment plants to operate at high coagulant doses and elevated pH thereby increasing the chemical dosage and sludge disposal costs.

When using alum as a coagulant, it has been found that the mechanism of coagulation varies with pH. At low pH (<5) charge-neutralisation by soluble cationic Al species is dominant, whilst at higher pH, sweep coagulation by $Al(OH)_3$ precipitates is more important (Lu *et al*., 1999). The same could also be said for Ferric salts with respect to the different modes of removal at pH < 5 and higher pH values (Duan and Gregory., 2003). Sweep coagulation occurs when raw water colloids become enmeshed in the metal hydroxide precipitates, it is one of the most widely used methods of destabilising a turbid suspension (Bache *et al*., 1999). In his work, they produced scanning electron micrographs of sweep floc coagulation. These showed raw water colloids (referred to as primary particles) were found to be covered by an adherent positively charged deposit which was attributed to the positively charged hydrolytic species. The remaining part of the precipitate showed evidence of mobility, and cohesiveness and was attributed to amorphous $Al(OH)_3$.

Sweep coagulation is more tolerant of departures from the optimum dosage conditions, which is a process control advantage. However its main disadvantage lies in increased coagulant demand, and increased production of sludge's which are difficult to dewater and cannot be sent to landfill and therefore have high disposal costs. Coagulant costs are also linked to the global economy and as such, need to be reduced as far as possible without compromise to water quality. This is one of the reasons that "charge neutralisation" may be a better operating approach as when the coagulant dose is optimised for the NOM, the quantity of coagulant and alkali dosed can be far less than for the same water utilising the "sweep flocculation" mode.

Part 2.7 The use Of Cationic Polyelectrolytes as Coagulants

The use of polymers in place of, or in conjunction with, the more conventional metal coagulants has been investigated since as early as 1979. Their mode of action is now reasonably well understood and can involve polymer bridging in the case of high molecular weight materials and charge neutralization and electrostatic patch effects with polyelectrolytes (Gregory, 1996). Polymers are reported to have particular advantages over metal coagulants for removal of NOM, mainly in the reduced solids formed because of the lack of solid hydroxide precipitate.

There is also a final water quality improvement reported. Their use as primary coagulants as well as the more traditional floc conditioning agents is well documented (Glaser and Edzwald, 1979; Jackson, 1980; Schlauch, 1981; Amy and Chadik, 1983; Rebhun *et al.*, 1984; Edzwald, 1986; Vik and Eikebrokk, 1989; Coccagna, 1989; Bolto, 1995). The performance of the coagulation process with polymers is less dependent on pH than with metal coagulants, there is a lower level of dissolved ions in the product water, there are no residual metal ions such as Al, Fe or Mn, and the alkalinity is maintained (Bolto *et al*., 1999). This has implications for the downstream processing of the process water, because of the lower content of insoluble solids present, processing is faster, filter runs are longer, the build-up of head loss is slower, a much smaller sludge volume is produced and the resulting sludge usually has a lower water content (Bolto *et al.*, 1999). However there are negative implications from using polymers and that is the potential long-term health effects on humans and the environment are largely unknown. There is also the possibility that the polymers may react with other water treatment chemicals such as those used in the disinfection process such as chlorine, ozone, or UV light which might lead to the presence of disinfection by-products in the final water. Some polymeric coagulants such as polyDADMAC have been noted to take considerably longer to form floc (Gregory and Yukselen, 2004) and therefore would require a treatment plant with a much larger footprint and embodied carbon, which would not be sustainable. Various polymers have been used in the water industry over the years. These polymers fall into two categories as mentioned above:

- Primary coagulants
- Flocculant aids.

Primary coagulants can act by charge neutralization, and they are generally speaking high molecular weight, high charge density compounds. Flocculant aids are polymers that are added after the primary coagulant, because of their abilities to modify the resulting flocs in such a way that improves their removal in the downstream processes. Determination of the charge density of the polymer is an important first step before optimising the dosage of the polymer as it has been proven that the charge density of a polymer is directly proportional to its efficiency at charge neutralisation. The charge density is a number expressed as units of charge per unit mass or volume, normally the unit is milliequivalents per gram or litre of polymer solution (meq/l).

The charge density of the polymer is usually expressed within a range by the manufacturer. The technique of colloid titration is a useful tool in determining the charge density of the polymer. Gregory and Kam, (1999) carried out a useful study, where they determined the charge density of various cationic polymers (whose cationic charge originated from quaternary nitrogen groups) using colloid titration and streaming current detection, and compared the results.

Colloid titration is based upon the stoichiometric interaction of two oppositely charged polyelectrolytes, or between polyelectrolytes and charged surfaces. In principal, when aqueous solutions of cationic and anionic polyelectrolytes are mixed, a neutralization reaction occurs, which is in many cases is stoichiometric with respect to units of charge. Colloid titration is dependent upon the strong binding of the titrant to the investigated colloid (Gregory and Kam, 1999). In the case of neutralization of an anionic polyelectrolyte by a cationic surfactant, the driving force is not only electrostatic but also of a hydrophobic nature (Gregory and Kam, 1999). The cationic polyelectrolytes were neutralized with potassium poly vinyl sulphate (PPVS), an anionic polyelectrolyte of known charge density. The end-point of the reaction can be determined visually, spectrophotometrically or by using the SCD technique, this is explained in more detail later in this section. Using the amount of PPVS required to neutralise the polyelectrolyte as detected by visual, spectrophotometric or SCD methods, the charge density of the polyelectrolytes can be calculated. Polyelectrolyte or colloid titration can in principle be carried out in two ways: as a direct titration with an oppositely charged polymer or as a back titration in which a defined amount of an oppositely charged polymer is added to the solution to be investigated and the excess is then titrated (Gregory and Kam, 1999). The latter method has been found suitable for use with anionic polymers using ortho-toluidine blue as an indicator. Interactions with potassium poly vinly sulphate (PPVS) and ortho-toluidine blue are well established and the end-point of the neutralization is easily detectable by a colour change of the indicator from blue to red-violet. This change can be monitored visually or by using a spectrophotometer at 635nm. Using the o-toluidine/PPVS system, cationic polymers can be determined directly and anionic polymers by back titration (Gregory and Kam, 1999).

For example, to determine the charge density of a well-known cationic polymer such as polyDADMAC using the visual method, the following procedure would be carried out:

- Add quantity of polymer to volumetric flask, dilute with distilled water if necessary
- Add a few drops of o-toluidine blue
- Titrate a quantity of PPVS into the polymer solution until the solution changes colour from blue to red-violet. This signifies the end-point.
- Using the fact that the PPVS solution charge density is known, the polymer charge density can be calculated simply.

Colloid titration can also be carried out using a UV spectrophotometer. The uncomplexed blue form of the ortho-toluidine blue has an absorption maximum at 635nm, but when the dye is bound to the PPVS, the peak in the absorption spectra shifts to 530 nm, this corresponds to the colour change observed visually, from blue to red-violet. By following the reduction in absorption at 635nm, the reaction can be followed. Streaming current detection can be used instead of visual and spectrophotometric methods to determine the end-point of charge neutralization i.e.: when the charge is equal to zero and neutralization is complete. Streaming current detection relies upon the streaming potentials and streaming currents that arise when solution flows through a capillary tube or a porous plug, when the surface of the material concerned is charged (Gregory and Kam, 1999). Counter ions in the diffuse layer adjacent to the surface migrate with the fluid, creating an electrical potential or current, which can be measured (Gregory and Kam, 1999). A typical arrangement for SCD has a sampling chamber, a reciprocating piston in a cylinder with electrodes and a signal amplifier, continuous samples taken from a point downstream of the coagulant addition flow through the sampling chamber. Colloids in the chamber momentarily adhere to the piston and cylinder surfaces. The cylinder is closed so that when the piston moves the fluid is set in motion through the annulus causing motion of the counter-ions relative to the attached colloids. The movement of charge corresponds to an electrical current, which can be amplified and read. This technique has been developed to allow automatic monitoring and adjustment of polymer dosage in solids conditioning and dewatering facilities to attain optimal operation (Abu-orf and Dentel, 1998). It has also importantly been developed for coagulant dosage control, via a feedback control loop arrangement.

Gregory and Kam (1999) found in their study, that the sharpness of the colour change of the cationic dye depended on the charge density of the polyelectrolyte. With lower charge density materials, the binding to PPVS was weaker and the binding of the dye to PPVS occurred before the neutralization of the polyelectrolyte charge had taken place. The method of streaming current detection has the advantage that the competitive interactions of PPVS and ortho-toluidine blue can be avoided, also the transition was very sharp at the iso-electric point. The results derived from the SCD method agreed very well with those from the spectrophotometry method. They also found that there was some loss of charge from the cationic polyelectrolytes at higher pH values, probably as a result of hydrolysis (Gregory and Kam, 1999).

These methods were used in another study carried out by Gregory and Kam (2001), the study investigated the interaction of humic substances with cationic polyelectrolytes. Adsorbed layers of humic substances, together with other organics, such as polysaccharides and polypeptides, give particles a negative surface charge (Hunter and Liss, 1982) and give enhanced colloid stability. Since natural organic matter is nearly always anionic over the usual range of natural water pH, it therefore interacts with cationic additives such as cationic polymers as well as hydrolysing metal coagulants such as ferric and aluminium hydroxide. The negative charge on humic substances originates mainly from dissociated acidic groups.

In the study of Hunter and Liss (1982), the charge densities of commercial humic acid and an aquatic humic extract were determined by studying their interactions with a series of cationic polyelectrolytes. It has been shown before, that the required dosage of additive is strongly related to the charge carried by the organic impurities (Bernhardt and Schell, 1993). The methods used to study the interactions were colloid titration by spectrophotometry and streaming current detection as described before and, flocculation determined by colour removal and use of a PDA 2000 optical monitoring method. The potential uses of using the PDA 2000 optical monitoring method are discussed elsewhere, however it is possible to derive information about the flocculation process from analysing the PDA derived flocculation curves.

Gregory and Kam (2001) also investigated the effect of pH on the charge density of two aquatic humic extracts. They found that each of the methods gave closely similar results for the humic acid charge density. They also importantly found that the charge density of the polyelectrolyte was related to the derived humic acid charge density. They found that a critical cationic charge density of around 3 meq/g is required to yield the maximum humic acid charge density. Above the critical charge density of 3 meq/g, it can be said that the interaction of the cationic polyelectrolytes and the humic acid is stoichiometrically one to one, but below that value this cannot be said to be true. Their work showed that optimum flocculation occurs at a polymer dosage very close to that required for charge neutralization. This means that as the cationic charge density is reduced, more polymer is needed to give optimal removal but, because of the non-stoichiometry mentioned above, less total cationic charge is required (Gregory and Kam, 2001). Their results also showed that the optimal degree of removal was considerably less for the low charge density polyelectrolytes than for the high charge density materials. The range of polymers investigated showed no indications that molecular weight played any part in the degree of removal, thereby suggestion that "bridging" mechanisms don't play a significant part in the process. Bridging mechanisms are discussed later in this literature review.

An earlier study carried out by Bolto *et al.*, (1999), evaluated the use of cationic polyelectrolytes in combination with hydrolysing metal coagulants for removal of NOM from reconstituted waters from different regions. The NOM was isolated and fractionated by adsorption on non-functionalised resins and an anion exchanger, and characterized by size exclusion chromatography before and after treatment. They followed the standard procedure for determining the optimum polymer dose, which was using jar tests in conjunction with UV_{254} and UV_{400} measurements. They used a selection of cationic polymers, such as polyDADMACS of varying molecular weight, polyacrylamides of high molecular weight, polymethacrylate of high molecular weight, chitosan, a weakly basic amino polysaccharide of medium molecular weight, and Alum.

They concluded that organic polymers on their own are not as good at colour removal as alum, the difference being 15% less colour removal with the polymers. Polymers with the least polar structure were usually the most effective at removing the hydrophobic fraction of NOM, the major component. Polymers perform better when there are particles present as would be the case in natural waters. Mixes of alum and polymer are a convenient way to introduce particles. They found that the alum dose could be reduced by 65% by the addition of a small amount of polyDADMAC to one of their water samples. Regardless of the water source, the same trend was found regarding removal of the different fractions. Hydrophobic acids were the most easily removed, followed by charged hydrophilic compounds and slightly hydrophobic acids were the hardest to remove. Some neutral hydrophilic compounds were removed to some extent by CPMA and poly DADMAC. Bolto *et al*. (1999) emphasised the need to understand the proportions of the fractions of NOM present in the water to be treated, as the removal efficiency can be enhanced by this knowledge. Costs may also be reduced if the metal coagulant demand could be decreased by usage of a small amount of polymer.

Part 2.8 Monitoring the Flocculation Process

When the term floc is used, it refers to the aggregates of particles that are formed in the coagulation/flocculation process. In some cases aggregates are already present in the raw water prior to treatment, and in these cases they can greatly influence the fate of particulate contaminants. The size and density of these aggregates are their two most important properties, as these two factors influence the efficiency of the subsequent processes such as sedimentation, filtration and flotation (Gregory, 1997). It is important therefore to have knowledge of these particular properties of the flocs/aggregates that are formed in the coagulation/flocculation stage, as the efficiency of this stage is crucial to the entire treatment process. It is also important to understand the factors that contribute to the size and density of flocs in the coagulation/flocculation stage. Factors such as the impeller type and dimensions, stirrer speed, vessel dimensions, pH, temperature, and type of flocculant/coagulant used, all have an effect on the physical and chemical properties of the flocs formed. Certain factors have a greater effect on the floc properties than others.

It is difficult to examine the properties of flocs using conventional laboratory methods, flocs are fragile and most intrusive techniques such as Coulter counters require that a sample is withdrawn through a small orifice thus causing breakage of the flocs. Particle counters do not give details on the structure of the flocs. Observing flocs under the microscope can give an idea of the structure of the floc, how open the structure is, or the average size of the floc but this technique is invasive and therefore increases the risk of floc damage. Several techniques have been developed that characterise flocs in different ways, using in-situ methods. In-situ methods also have the greatest potential to be taken to the water treatment plant where there output is needed the most. Figure 2 shows the PDA 2000 optical flocculation equipment.

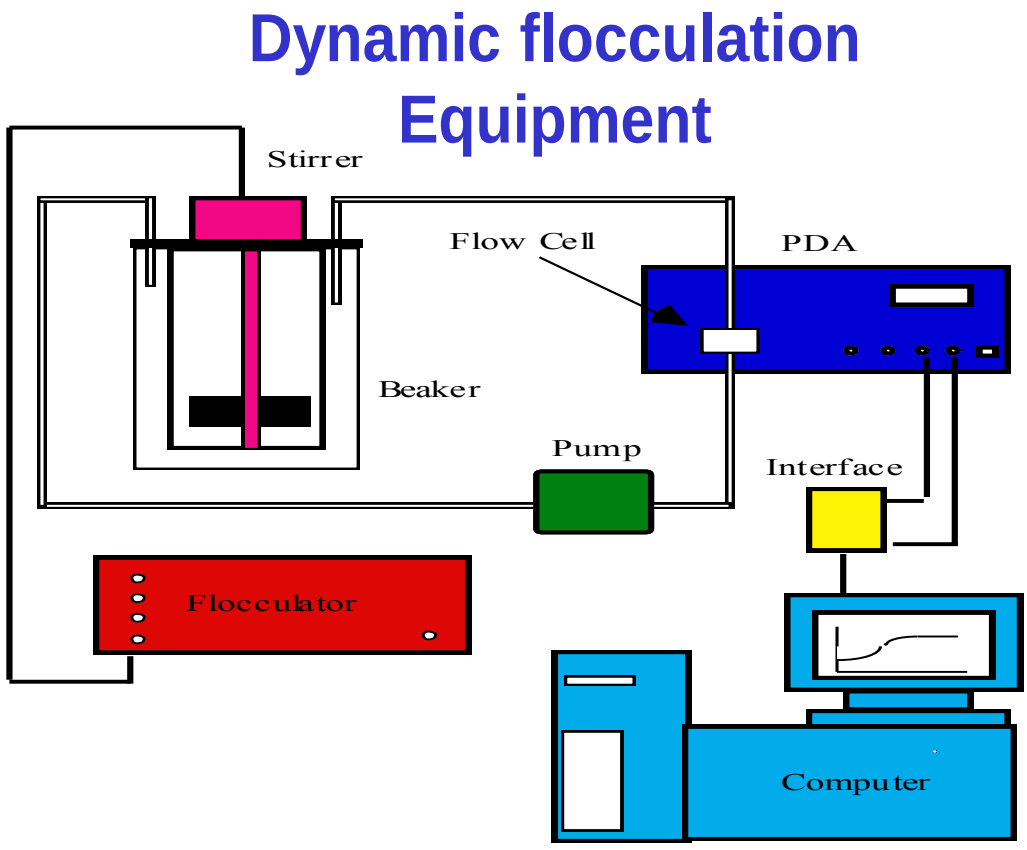

Figure 2 Dynamic flocculation monitoring equipment using the PDA 2000

The PDA 2000 measures the average transmitted light intensity (dc value) and the rms value of the fluctuating component passing through narrow tubing containing the flocculation sample liquor. The ratio (rms/dc) provides a sensitive measurement of the particle aggregation (Gregory and Nelson, 1986). This ratio is known as the flocculation index or FI. This technique has been used in many studies to monitor the flocculation process. More recently, it has been used to characterise the strength of flocs formed during the coagulation/flocculation process. Using this method, coagulation/flocculation can be carried out with a variety of metal hydrolysing coagulants and or polyelectrolytes. The flocs made by different coagulants or polymers, under different stirring regimes grow to different sizes. This can be represented by the PDA 2000 as differences in FI value but are only comparable within the same jar test system as the floc index is dependent to on the conditions in which the floc was formed. Studies on the strength of flocs can be carried out with this equipment by inducing breakage of the fully formed flocs, followed by studying the extent of the regrowth of the floc. The floc strength factor can be calculated as mentioned in part 2.9, and this gives a comparative quantity (within the same shear system) of the aggregate strength. From determining the extent of the regrowth of the flocs, it is possible to gain some idea of the reversibility of the floc breakage. This technique can be used alongside the UV_{254} absorbance removal method to determine optimal flocculation conditions corresponding to optimum colour removal.

This technique was used by Gregory and Yukselen (2004) in an investigation into the effects of rapid mixing on the break-up and re-formation of flocs. It is well known that mixing conditions can have a very significant effect on the performance of coagulants and flocculants. Too rapid mixing in the floc growth phase can give rise to smaller flocs formed. Smaller particles have been shown to cause the most removal problems within the treatment process (Rajagopalan and Tien, 1976). However, it is equally important to mix sufficiently so that the coagulant/flocculant is well dispersed, otherwise its performance will be affected and wastage of coagulant can occur. The rate of mixing controls to some extent the particle collision process that is required for the formed flocs to grow into larger aggregates. In the case of charge neutralization or polymer bridging, rapid mixing is especially important since poor mixing can lead to localized over-dosing and re-stabilisation of some particles.

When using hydrolysing metal coagulants, the formation of hydrolysis products is very rapid, but competing processes, such as adsorption and precipitation, could depend on mixing conditions (Amirtharajah and O'Melia, 1990). It has been suggested that initial mixing conditions are not so important in the case of sweep flocculation but this is not well established (Amirtharajah and Mills, 1982). After coagulant dosing and mixing, flocs grow initially at a rate that is determined mainly by the applied shear, the particle concentration and the collision efficiency (Gregory and Yukselen, 2004). As the flocs become larger, further growth is restricted by the applied shear force for mainly two reasons. Existing flocs may be broken as a result of disruptive forces (Blaser, 2000) and the collision efficiency of particles in a shear field becomes lower as the particle size increases (Brakalov, 1987). However, there is a dynamic balance between floc growth and breakage thus leading to development of a steady-state floc size distribution, where the limiting size is dependent on the applied shear rate (Muhle, 1993). When flocs are subjected to an increased shear rate, breakage can occur. The full nature of this breakage is not well understood but it is thought to occur by two main processes of surface erosion and large-scale fragmentation as described in part 1.9. For most flocculation monitoring methods, surface erosion and large-scale fragmentation are almost indistinguishable. Flocs may rupture into roughly equal sized fragments, or small particles may be eroded from the surface of the floc. In turbulent flow the mode of breakage depends on the floc size relative to the turbulence microscale (Muhle, 1993). The extent of the breakage depends greatly on the intensity of the shear applied and on the floc strength, a difficult characteristic to measure. It has been observed that after floc breakage, re-growth may occur once the original low shear conditions have been restored. However in some cases floc breakage may be irreversible and only limited regrowth may occur (Francois and Van Haute, 1984). Where the floc is comprised of NOM and a hydrolysing metal coagulant, the removal is known not to be good with respect to the hydrophilic component which is also known to be highly charged. There are perhaps parts of the NOM floc that contain areas of increased repulsion. This may explain the reluctance of NOM floc to re-grow.

It is therefore important to study the effect of mixing conditions on the breakage and reformation of flocs. In the study carried out by Gregory and Yukselen (2004), clay suspensions were used along with alum and a cationic polyelectrolyte as coagulants.

Their results using alum, found that the formation of flocs was greatly influenced by the duration of the rapid mixing phase at 400rpm. In all cases the FI value reached a plateau value rapidly, but the plateau value was considerably higher for the shorter durations of rapid mixing. They found that floc breakage could be completed in 10 seconds of rapid mixing at 400rpm. Importantly their results showed the previously reported effect by Gregory and Rossi (2001), that the final floc size after breakage is a function of the breakage conditions and not the mode of floc formation. This was deduced from observing that the FI values after breakage were nearly the same for all cases. When the same tests were carried out using the cationic polyelectrolyte, polyDADMAC very different FI curves were obtained. The onset of flocculation occurred considerably later than with alum, and a longer duration was required for the FI values to reach the plateau value. The flocs formed were considerably larger than those with alum but the rapid mix duration affected the plateau value less than with alum. Longer rapid mix times gave rise to earlier onset of floc growth by increasing the rate of adsorption of the polymer. The floc breakage duration was increased to 30secs to break the flocs fully. The re-growth after breakage was considerably higher than with alum, suggesting that the flocs were stronger.

Part 2.9 Measurement of Floc Strength and Breakage Mechanisms

Floc strength is a particularly important measure to quantify as due to the nature of the water treatment process, the floc will be subjected to many different shear fields as it passes from the flocculation stage to the solid/liquid separation stage of filtration. The likelihood of experiencing regions of high shear is high (McCurdy *et al*., 2004). The ability of the floc to withstand shear is therefore considered to be of great importance and it is this measure that is of heightened operational importance when optimising process performance to minimise the break-up of floc, as it is known that smaller particles generally have lower removal efficiencies (Boller and Blaser, 1998). Floc strength is directly related to the floc structure, and is therefore highly dependent on the floc formation process, as the floc strength is thought to be dependent on the strength of the inter-particle bonds within the aggregate (Parker *et al*., 1972; Bache *et al*., 1997). The method of quantifying floc strength has proven difficult due to many factors:

- Floc structure is complex
- Flocs are fragile (intrusive monitoring techniques must not damage the floc)

- Floc size is not spherical or regular
- Floc composition varies greatly

Another complicating issue due to the above factors is that there are two generally accepted methods of floc rupture (Parker et al., 1972; Francois, 1987; Yeung and Pelton, 1996; Mikkelsen and Keiding, 2002). These two methods are:

1. Surface erosion – removal of small particles from the floc surface resulting in an increase in the small particle size ranges.
2. Large scale fragmentation – breakage of the floc into pieces of a similar size without an increase in primary particle concentration.

The two breakage modes described above are thought to arise from different shear stresses (Yeung and Pelton, 1996). Surface erosion is thought to arise from the action of shear stress acting tangentially to the floc surface whilst fragmentation is thought to arise from the action of shear stress acting normally to the floc surface. Fundamentally, floc formation and breakage within a flocculation suspension is governed by the prevailing shear conditions and will reach a steady-state. When the shear rate increases above a certain critical level, flocs will break until a new steady state is reached (Jarvis *et al*., 2005). There are two approaches to quantifying floc strength, these are as shown in table 2:

1. Macroscopic – these are focused on considering the system as whole and the energy required within the system to achieve floc breakage.
2. Microscopic – these are focused on measuring the strength of the inter-particle forces within the floc.

Of the two types of technique, the impeller type is considered popular having been used by many researchers in the study of synthetic or "model" waters (Leentvaar and Rebhun, 1983; Francois, 1987; Spicer *et al*., 1998; Bouyer *et al*., 2001; Bache and Rasool, 2001; Gregory and Dupont, 2001; Fitzpatrick *et al*., 2003). The impeller type and vessel dimensions were different between the systems so comparison between systems is difficult as the energy dissipated would not be the same for each system. This is one of the draw-backs to this technique.

The method of monitoring the floc before and after the breakage period is also different between the systems, with some researchers preferring particle sizing devices, and some using video camera analysis. One of methods used was that of observing the effect of increased shear stress on the floc size within a vessel, and this technique which has been used by Fitzpatrick *et al*. (2003) involved using the PDA to quantify the floc index before and after breakage to calculate the floc strength factor according to:

Floc strength factor = d_2/d_1

Where d_1 = floc index before breakage, and d_2 = floc index after breakage

This method has been used to monitor synthetic or model waters reasonably extensively, but there is little research on the use of the PDA monitored impeller type breakage method when using natural raw and treated water.

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Strength Technique *Macroscopic*	Description
Impeller	Exposure of floc to single level of increased shear within a vessel, and comparing ratio of floc size before and after breakage (Francois, 1987; Fitzpatrick *et al*., 2003) Exposure of floc to increased levels of shear at a controllable rate within a vessel, and measuring the energy input for floc breakage (Leentvaar and Rebhun, 1983; Francois, 1987)
Ultrasonics	Application of a controllable ultrasonic field to a floc suspension and observing floc erosion (Wen and Lee, 1998; Chu *et al*., 2001)
Multigrid mixer	Floc exposed to hydrodynamic stress from a controllable oscillatory mixer (Bache *et al*., 1999). Flocs placed in a vibrating column and subjected to various amounts of oscillation, and the vibration is converted into energy requirement.
Microscopic	
Micromechanics	The breaking force required to pull apart a single floc in the tensile mode (Yeung and Pelton, 1996)
Micromanipulation	The squeezing of a single aggregate in suspension between a glass slide and a fibre optic probe until floc breakage using a force transducer (Zhang *et al*., 1999)

Table 2 Review of techniques for determining floc strength (adapted from Jarvis *et al*., 2005)

Floc characteristics such as size are strongly influenced by the prevailing hydrodynamic conditions, and one important method of comparing systems with a known floc size distribution is the comparison of the floc size in contrast to the eddy size. The theory suggests that turbulent energy as present in flash mixers and other mixing devices, is dissipated by eddy vortices and viscous shear

The Kolgomoroff microscale (λ) represents the smallest practical size of an eddy for given mixing conditions (Levich, 1962; Parker *et al*., 1972). This microscale shows the approximate scale above which energy dissipation from viscous water motion is predominant (Clark and Flora, 1991). Equation 1 shows the expression for the microscale of turbulence λ:

$$\lambda = \left(\frac{\mu^3}{\varepsilon}\right)^{1/4} \text{ where } \varepsilon = G^2 \upsilon$$

Equation 1

λ = m

υ = m s^{-1}

μ = kg m^{-2} s^{-1}

G = s^{-1}

ε = N m $s^{-1}$$kg^{-1}$

Where ε is the average energy dissipation within the vessel, μ is the viscosity, ν is the kinematic viscosity, and G is the average velocity gradient in the vessel. This can be of practical use when identifying the breakage mode of flocs when they have been subjected to high shear rate conditions. Flocs that are larger than λ are exposed to viscous shear forces and may therefore undergo large-scale breakage (fracture or fragmentation), whereas flocs that are smaller than λ may be entrained within eddies and instead of large-scale breakage, particles are eroded from the floc exterior as it rotates in the eddy (surface erosion). It is postulated that flocs will reach an equilibrium size around the microscale of turbulence (λ), unless bonding forces within the floc structure can prevent large scale fracture (Boller and Blaser, 1998; Ducoste and Clarke, 1998). Comparison of the floc size to the microscale of turbulence (λ) can therefore give an idea of the likely mechanism of floc breakage.

Part 2.10 Jar Test Parameters

The jar test is commonly recognized throughout the water industry as the most valuable and most used tool for simulating coagulation conditions on a full-scale water treatment plant. This test usually involves simulating the full-scale plant primary treatment steps within a single vessel. This test can be used to evaluate the effects of changes in coagulant dose, pH, temperature, mixing intensity, and many other variables on the removal of particulates, NOM and turbidity. In order to accurately simulate the full-scale plant conditions, it is important to model the hydraulics of the treatment steps realistically. Key parameters include:

- Velocity gradient in mixing unit
- Retention time within the mixing unit
- Velocity gradient within the flocculation unit
- Retention time within the flocculation unit

Particular importance should be placed upon accurately simulating the velocity gradient within the jar tests as it is known that the intensity of rapid mixing affects the characteristics of flocs, notably the floc strength (Gregory and Yukselen, 2000). Velocity gradient is usually expressed as G with units of s^{-1}. The velocity gradient is calculated using the energy dissipation rate in the fluid, or it can be interpolated from calibration curves. In order to achieve comparable jar test results with those generated from full scale plant, it is important that the velocity gradients should be similar or to at least note the differences between the two systems when interpreting the results. There are usually three stages in the jar test process, corresponding to the initial treatment phases on a full scale plant. These are:

1. Initial rapid/flash mix – The purpose of this stage is to disperse the primary coagulant into the raw water in a fast and uniform manner. This helps to optimise the coagulation process. The duration of the rapid mix period should be equivalent to the retention time in the plant mixing unit if results are to be comparable.

2. Flocculation – This refers to the period of gentle mixing that occurs in the plant flocculators. Particles that have been destabilised in the coagulation process are allowed to coalesce into larger particles called flocs. At this stage it is possible to add polymeric flocculant aids in order to generate floc that is easily removed in the downstream clarification/flotation stage. This could prove difficult as the addition of flocculant would require adequate mixing without significant floc break-up.

3. Sedimentation – This refers to the removal of the flocculated matter by gravity in sedimentation basins or clarifiers. The most important parameter is the surface loading or overflow rate. The surface loading rate is determined by dividing the basin flowrate by the surface area, a further unit conversion shows that the surface loading rate corresponds to a velocity. This velocity is equivalent to the particle settling rate.

It is usual to assess the performance of the jar test for surface waters containing NOM by measuring the UV_{254} absorbance removal and the turbidity removal. UV_{254} absorbance removal gives an indication of the extent of organic substance removal as mentioned earlier, and settled turbidity gives an indication of particulate removal. UV_{254} absorbance is generally thought of as a more accurate measure of coagulation performance for water with significant NOM content.

Part 2.11 Overview of Filtration

Filtration is the process within the water treatment process that removes particulate matter in the form of fine suspended solids from the water, thus improving the final water quality. Particulate matter can include flocculated humic material, oocysts and other solids present in surface or ground waters. Filtration is usually achieved by the influent water flowing downwards or upwards through a bed of porous media. The filtration unit can be classified according to the type of porous media used, the rate of flow and the mode of inducing the hydraulic gradient across the filter in order to achieve flow. Flow through the filter can be achieved by gravity, in which case the filter is open to the atmosphere and is termed a gravity filter, or the filter can be closed to the atmosphere and operate under pressure; this is termed a pressure filter. There are two main types of filter in industrial use (excluding membrane filters), these are Slow Sand Filters (SSF) and Rapid Gravity Filters (RGF). The most common filter in use in the developed countries is the RGF. Slow sand filters operate at low filtration rates where most of the solids are removed in the top few cm's of the sand bed usually by biological action within the Schmutzdecke layer. Generally slow sand filtration in the USA uses flow rates up to 0.4 m/h and doesn't involve the addition of pre-treatment agents such as coagulants (Cleasby and Logsdon, 1991).

Rapid gravity filters operate at higher filtration rates and the solids are removed within the granular bed via a number of mechanisms, a process termed *depth filtration (*Amirtharajah, 1988). After a period of operation referred to as the *filter cycle,* the filter becomes clogged with removed particulates and must be cleaned. Rapid filters are cleaned by back-washing, using an upward, high-rate flow of water. Slow sand filters are cleaned by scraping off the dirty layer from the surface (Cleasby and Logsdon, 1991). The filter effluent water quality can be monitored online using turbidimeters, particle counters, the advantages and disadvantages of both of these methods of monitoring are discussed further in this section in part 2.17. In some cases cryptosporidium monitoring can be carried out on filter outlets by means of passing a sample of the filtered water through a cryptosporidium cartridge, and subsequent analysis in the laboratory.

In the UK, the Drinking Water Inspectorate (DWI) sets the regulatory limits for filter outlet turbidity based on the associated risk of passing potential pathogens through the filter as the effluent turbidity increases. Filtrate turbidity above the regulatory target is associated with increased risk of cryptosporidium oocysts and other such pathogens passing through the filter. It is for this reason that filtered water quality must be monitored using reliable online instruments, and the correct operational procedure followed should a breach of the turbidity alarm limits occur. Filtration is generally seen as the most vital part of the solid removal process of surface water treatment, as the ultimate factor for determining the correct coagulation conditions is how well the filtration stage removes the resulting flocculated material. The process for coagulation optimisation therefore should consider all of the stages of coagulation, flocculation and filtration inclusively. Many different studies have been carried out into the various methods of optimising filtration performance but currently there are few studies that have looked into optimization of coagulation, flocculation and filtration using jar test techniques such as the PDA optimised jar test procedure and pilot and full-scale plant trials. There has been considerable work carried out into the processes that occur during rapid gravity filtration and it is fair to say that the factors effecting filter performance have been reasonably well qualified. It is useful to consider the basic filtration processes that occur during rapid gravity filtration

Part 2.12 Filtration Processes

The processes that take place within the filter bed have been well researched, and good understanding of the concepts of the filtration process has been achieved. It is known that filter performance is influenced by many factors such as the physical and chemical characteristics of the filter media and suspension, as well as the physical configuration of the filter itself and how it is operated. Depth filtration refers to particle removal by attachment to the filter media, or to previously retained particles. During the initial stage of the filter run there are few previously retained particles and so the filtrate quality is poor during this period, this is referred to as the ripening phase. Several important theories were developed in the 1970's and 1980's concerning particle attachment theory by Ives (1969). Amirtharajah (1988) wrote a comprehensive review on filtration mechanisms.

Amirtharajah (1988) stated that the particles attach to the filter media via three mechanisms:

1. Electrostatic interactions
2. Van der Waals forces
3. Chemical interactions

However, before the particle can attach to the media it must first be transported from the bulk suspension. It has been shown by Ives (1969) that if the particle is to be attached to the media then it must cross through the fluid streamlines around the media grains via five mechanisms:

1. Interception – particles of a finite diameter, e, which follow streamlines that come within e/2 distance from the grain surface will contact the surface, and adhesion will take place.
2. Diffusion – diffusion occurs according to Brownian motion if the particle is very small (1μm).
3. Inertia – Particles travelling with a certain velocity may tend to travel in straight lines and therefore cross the fluid streamlines and deposit on the grain surface. This effect has been shown to be negligible in water systems (Ives, 1960).
4. Sedimentation - gravitational forces such as Stokes settlement, if the particle is large (>5μm) and appreciably denser than water.
5. Hydrodynamic - caused by the velocity distribution within the filter pores, which together with the shape of the particle cause it to rotate and translate across the flow field (Ives, 1980).

The mechanisms for transport of a particle from bulk suspension to the surface of a media grain are not exclusive, and several may act simultaneously on any particle at any time.

Once the particle is transported and attached to the media, it can serve as a collector for further particles. It is clear that for effective filtration, the filtration conditions must be conducive to transportation of the suspended particle to a potential collector site and attachment of the particle to the collector. In real situations, the particle size range entering the filter is likely to include different particle sizes and shapes and therefore optimisation is complex. In practice the particle size distribution entering the filtration stage is unknown as turbidity measurement is the most popular measurement of the water quality at this stage, which bears little correlation to particle size. It is thought that physical mechanisms are mainly responsible for transportation of the suspended particle onto the collector site, and chemical conditions dominate the attachment processes (Darby and Lawler, 1990). Some very useful conclusions were drawn from a controlled study on the effect of particle size on removal and head loss carried out by Darby and Lawler, 1990 using latex spheres. These were:

- Particle removal increased with depth.
- Preferential removal of certain particle sizes was evident.
- Substantial evidence of floc formation and break-off was found. Individual particles attached and then acted as collectors before being subsequently broken off as a new particle aggregate with a new size and characteristics.
- The highest increase in hydraulic gradient occurred in the top section of the bed

Overall the filtration process is inherently an unsteady-state process that is greatly dependant on the physico-chemical properties of the suspension to be filtered and the operational conditions. Whilst the filtration processes are essentially unsteady-state, there are different stages within the filter process that are distinctive and important to understand when trying to optimise filter performance.

The *filter cycle* can be broken down into three distinct stages:

1. Filter ripening sequence
2. Baseline filtration
3. Run termination on high headloss or decrease in filtered water quality

It is important to understand the main factors that affect the filter cycle as it is then possible to optimise the filter performance and increase the efficiency of the overall water treatment process. There has been considerable research into methods for reducing the duration or intensity of the filter ripening stage as it is important to understand the connection between the backwashing process used and the forward flow performance as the two are very much interrelated. Work by Colton *et al*., (1999) found that ripening is very important in minimising breakthrough of particles in the 2-5µm size range, as up to 40% of the particles that pass into supply during a 48 hour run, do so in the first hour of the run. This work also found that the severity of the filter ripening breakthrough can be minimised by the backwash method and by incorporating a slow-start.

Another method of minimising the impact of ripening is to incorporate a period of "run to waste" at the start of the run until the quality improves. The period of "run-to-waste" can be incorporated into the filter run sequence and is affected greatly by the efficiency of the ripening process and it therefore important to minimize the extent of the ripening stage as it is wasteful because the water passing through the filter at this time is poor quality and shouldn't be put forward into supply. It is generally acknowledged that filter backwashing methods have a great impact on the filter ripening sequence and it is very important to remove as much of the backwash material as possible in most cases. It is also important that the backwash process itself has been adequately designed for the specific filter media and temperature conditions.

Part 2.13 Filter Media Properties

Filters are used for many different removal processes within the water treatment process, these are summarised below:

- Removal of chemically or biologically oxidized iron and manganese (from groundwater sources)
- Removal of flocculated material generated by coagulants and flocculants (surface water treatment)
- Removal of pesticides and other trace organic contaminants (adsorption onto GAC)

For these many applications, different media are used to give beneficial performance depending on the function of the filter. There are many different types of filter media used in the water industry, and each type has its own particular benefits and the choice of media will depend on many different factors. Table 3 below shows the different media types used in the water industry along with their physical properties.

Media	**Purpose**	**Grain density (kg/m^3)**	**Loose-bed porosity**	**Sphericity**
Silica sand	1st stage filtration	2650	0.42-0.47	0.7-0.8
Garnet	1st stage filtration	3600-4200	0.45-0.55	0.6
Granular activated carbon	2nd stage adsorption of organic contaminants	1300-1500*	0.5	0.75
Anthracite	1st stage filtration	1450-1730	0.56-0.6	0.46-0.6
Crushed recycled glass	1st stage filtration	2511	0.5	0.7

Table 3 Typical Properties of Filter Media (Cleasby and Fan, 1981; Dharmarajah and Cleasby, 1986; Cleasby and Woods, 1975; Fitzpatrick, 2005)

*Virgin carbon only

It is common to use dual and triple media combinations of silica sand and anthracite and silica sand, anthracite and garnet respectively. Granular activated carbon or GAC has been used in groundwater sources for reducing taste and odour compounds in granular beds that operate as filters and adsorbers (Graese *et al*., 1987). The most common use of GAC in surface water treatment is a separate stage after the rapid gravity filtration process. The primary purpose of GAC treatment in this case is adsorption of organic compounds such as pesticides. It has also been known to use biologically activated carbon filtration to remove both pesticides and NOM. In this case, the biological activated carbon filters were supplementary to conventional sand filtration. This process is used in Amsterdam, and it has been found to be a very effective method of removing residual DOC with particular reference to pesticides (Hoek *et al*., 1999). There are several properties which help to define media and which must be taken into account when designing the filtration unit, these are:

- Grain size and size distribution – this is defined by sieve analysis. This plays an important part in filtration efficiency and backwash requirements. The effective size or d_{10} is that size for which 10 percent of the grains are smaller by weight, this can be read off log-probability plots of the sieve analysis. It is normal to report both d_{10} and the overall size range of the media.
- Grain shape and Roundness – the shape and roundness of the filter grain dictate the backwash flow requirements, the fixed bed porosity, headloss through the media, and filtration efficiency (Cleasby and Logsdon, 1991) . Chemical engineering literature defines the sphericity (ψ) as the ratio of the surface area of an equal volume sphere of diameter d_m to the surface area of the grain (McCabe and Smith, 1976). It is possible to calculate the sphericity by rearranging the Carmen-Kozeny equation for pressure drop in a packed bed and this is discussed later in this section.
- Grain density or specific gravity – the mass per unit grain volume is the measure of grain density. This property greatly affects the backwash requirements as grains with a higher density and the same diameter require higher upflow rates in order to achieve fluidisation.

- Grain hardness – This property reflects the ability of the media to withstand high shear forces that will act on it during the backwash process and general "wear and tear" during the filtration process. Hardness is usually described by the Moh hardness number, which is a scale of comparative hardness of one mineral to another. Generally anthracite and GAC have the lowest hardness of the materials used in the water industry. Both of these compounds are friable and will wear away as the media is put to use. Although GAC is more friable than anthracite, the progressive reduction that takes place in its grain size due to backwashing and regeneration has not been reported to be a significant problem in practice (Graese *et al*., 1987).
- Fixed-Bed Porosity – This is expressed as the ratio of the void volume to the total bed volume. This property affects the backwash flow rate, solid holding capacity of the bed, and fixed-bed head loss. This factor is determined partly by the geometry of the grains; angular grains (with lower sphericity) have a higher fixed-bed porosity (Cleasby and Fan, 1981). In the case of a low uniformity coefficient it is possible for small grains to nest within the pores of the larger grains thus reducing the overall porosity. The fixed-bed porosity is easily calculated by placing a known amount of media (mass and density known) into a tube of known internal diameter. The volume of the grains is calculated by dividing the mass by the density, and the total volume is the volume taken up by the media in the column. The void volume is therefore the bed volume minus the grain volume. When using pilot filter columns, it is important to ensure that the diameter is at least 50 times the grain size of the coarser grains to minimize wall effects. These wall effects are caused by pockets of higher porosity occurring near the wall of the filter which therefore increases the average bed porosity higher than it would be in a conventional full-scale filter (Cleasby and Logsdon, 1991).

Overall, a lot of aspects of filter media properties need to be considered when designing a filtration unit. Other considerations are cost, filtration flow rates and backwash system capability. The influent water quality is also a consideration, and is considered next.

Part 2.14 Physiochemical Properties of Floc and Filter Performance

The importance of adequate particle de-stabilisation with respect to NOM removal has already been discussed in the coagulation section of the literature review, and now it is logical to consider the importance of floc characteristics on filter performance. Firstly it is important to establish the nature of the colloidal and non-colloidal material requiring removal within the treatment process. It is important to identify effects that might change the nature of the raw water and therefore may effect filter performance. The attachment of floc to media grains should only happen when the attractive London – Van der Waals force is greater than the electrical repulsive forces. It is logical to say that if the reverse is true, then all things being equal, attachment won't occur. This can be expressed by equation 2:

Equation 2

$\eta_R = \alpha\eta_T$

η_R – Dimensionless deposition or removal rate of particles

η_T – Dimensionless transport rate

α - Attachment efficiency

The attachment efficiency accounts for the chemical-colloidal effects on the rate of particle deposition, and η_T accounts for physical effects (O'Melia and Stumm, 1967). In this way, it is possible to see that for deposition to occur, the chemical-colloidal interactions must be favourable. In this instance the attachment efficiency approaches unity, and the deposition rate is equal to the transport rate (Elimelech and O'Melia, 1990). On the reverse side, when the chemical-colloidal interactions are unfavourable, the attachment efficiency is less than one, and particle deposition is hindered. Analytical expressions have been derived for η_R and η_T, and these are shown below:

Equation 3

$\eta_T = 4.0A_s^{1/3}Pe^{-2/3}$

where A_s is a porosity dependant parameter of Happel's porous medium model (Happel, 1958). Pe is the Peclet number defined as $2a_cU/D_\infty$; a_c is the diameter of the spherical collector, U is the approach velocity of the suspension towards the collector, and D_∞ is the diffusion coefficient at infinite separation. A theoretical expression for the attachment efficiency (α_{the}) was derived by Spielman and Friedlander (1974).

Equation 4

$$\alpha_{the} \equiv \left(\frac{\beta}{1+\beta}\right) S(\beta)$$

Where β is an analytical expression that depends on the total colloidal interaction energy and S(β) is a slowly varying function of β with tabulated values given in Spielman and Friedlander (1974). The theoretical side of particle deposition on porous media has therefore been well researched and useful correlations obtained. However, the theoretical system cannot answer the question of whether a suspension containing real floc will filter well. A new concept of filterability was developed by Ives (1978), and was designed to practically address the issue of whether the media in question would filter the influent suspension, or whether the resulting suspension is filterable. The result of the work which involved pilot filtration apparatus was the derivation of a dimensionless Filterability Number F:

Equation 5

$$F = HC/vC_0t$$

H – Head loss after time t

C – Filtrate concentration

C_0- Influent concentration

v – approach velocity (volumetric flowrate per unit face area)

The numerical value of F is not informative by itself, but a comparison of F for the same suspension and different treatment parameters (such as pH) enables the relative filterability of different pilot trials to be assessed. In this manner, Ives (1978) illustrated, using jar test and pilot filter experiments that is was possible to assess the effect of velocity gradient on the filterability of the suspension. The problem with this method is that the measurement of particle

concentration is extremely difficult and the most common method of measuring particle concentration is turbidity. As mentioned previously, turbidity is not an absolute measure of particle size distribution, concentration or the state of charge neutralization achieved. The unsteady state nature of filtration also causes problems for assessing the filterability number as the filtration conditions would have to be identical and comparisons made at equivalent stages within the filter run. Other researchers such as Cleasby (1969) have derived models to determine filterability coefficient. Ives (1978) and Cleasby (1969) determined values at pilot plant scale and full scale, respectively. All of these models are however not plant operator friendly as they are time consuming and with increasing demands on resource time, there is more emphasis placed on less time-consuming tests.

There is currently no quick universally applicable test that a plant operator can perform on the raw water that will identify the optimum conditions for good filterability. Some researchers have progressed further into the field of understanding the relationship between floc characteristics and filtration performance by identifying zeta potential as the main parameter, and optimising systems on this basis. In theory, the zeta potential of well destabilized particles has been reported to be -4 to +3 mV (Amirtharajah and Tambo, 1991). Some researchers have reported a wider band of operation for good filter performance. An optimum band of +2 to + 4 mV was reported for alum coagulation at pH 6.0 and -4 to + 4 mV at pH 7.4 (Gregory and Carlson, 2003). They also confirmed that the rate of floc formation (as measured by using the PDA and jar tests) was indicative of overall process performance. The work of Sharp *et al.* (2004) is also worth noting at this point because they found that the optimum zeta potential range for effective coagulation (determined by removal of NOM) was -10 to +3 mV. It would seem that the optimum zeta potential range is rather system dependent and something that should be optimized for a particular water treatment system. It would seem to vary with the chemical nature of the colloidal species of the water and the coagulants and pH conditions used. It is useful to see that it is possible to optimise filter performance based on zeta potential, and this is something that requires further exploration.

The surface charge of the floc has been shown to play an important part in the attachment of floc to media, and it is useful to consider what effect the physical condition or strength of the floc has on the filtration processes. The ability of certain polyelectrolytes to form "strong" floc is well known, and it has been suggested that they filter well because they are more resistant to the high shear stresses found within the filter bed than conventional floc formed using metal hydrolysis products (Tien and Payatakes, 1979). It has also been suggested that the use of polyelectrolyte can aid collector efficiency due to the formation of particle-polymer-particle bridges (LaMer and Healy, 1963). It could also be possible that the term "weak floc" may apply to poorly charge-neutralised floc, in which case the solution would be to optimise the coagulation conditions before applying polyelectrolyte dosing. Poorly coagulated floc would not be expected to filter well as the attachment efficiency would be lowered due to unfavourable chemical-colloidal interactions. This could apply to the filters at Albert WTW, and may explain the breakthrough observed at low headloss. In some situations, the application of polyelectrolyte may be the most cost-effective solution to certain filtration problems.

Part 2.15 Backwashing Regimes

At the end of the filter run or when it has become apparent that the filter is clogged with deposits, it is normal practice to clean the filter using an upflow of water and air combinations. This process is known as backwashing and it is designed to remove the clogging deposits that have collected in the filter bed. Backwash procedures vary but all include the reverse flow of water. Reversing the flow of water in a rapid gravity filter will eventually have the effect of fluidising the media as the upflow rate is increased. The degree of fluidisation is usually one of the design parameters in the backwash system. The incorporation of air scour into the backwashing procedure is now commonplace. It is known that the use of air scour on its own is not efficient at agitating the depth of the bed and is more useful in disrupting the surface in the case of the formation of a surface mat. The efficiency of backwash is very important as it has been shown to affect the immediate effluent quality of the next run (Cleasby *et al*., 1975, Amirtharajah, 1993). It has been shown that combinations of air and water at flow rates that give rise to *collapse-pulsing* give the best cleaning (Amirtharajah, 1984). Researchers have shown that the use of water alone is an inefficient cleaning process, as a fluid film around the grains minimizes grains collisions and attrition (Cleasby *et al*., 1977, Amirtharajah, 1978).

The choice of backwashing system depends on the filter configuration, the water type and treatment process and all of these factors should be taken into account when deciding the backwash regime. A theoretical equation for collapse-pulsing was developed by Amirtharajah (1984), and is shown below:

Equation 6

$$0.45Q_a^2 + 100\left(\frac{V}{V_{mf}}\right) = 41.9$$

in which Q_a is the airflow rate in cubic feet per minute per square foot, and V/V_{mf} is the ratio of the superficial water velocity divided by the minimum fluidization velocity based on the d_{60} grain size of the medium. Hewitt and Amirtharajah (1984) went on to formulate an empirical design equation to predict the flow conditions required to achieve "collapse-pulsing".

Equation 7

$$\%\left(\frac{V_W}{V_{mf}}\right) + aV_A^2 = d$$

where a = 8.5 and b = 43.5 for sand, V_A air velocity (m/min).

Fluidisation of the media occurs when the upflow fluid forces balance the gravitational drag forces of the media grains. Upflow velocities are usually expressed as a percentage of the minimum fluidisation velocity (V_{mf}). A review of backwashing filters with air scour was carried out by Amirtharajah in 1993. He reported on different air flow patterns occurring with increasing water upflow and constant air flow. He found that at low upflow (<10% V_{mf}) the air bubbles moved through the media with very little disturbance to the media grains. At 10 -20% minimum fluidisation velocity air cavities form and expand, and at 25-30% minimum fluidisation velocity the air cavities formed on top of each other causing the lower cavity to collapse this giving rise to the term "collapse pulsing". The latter caused the greatest amount of attrition between the grains and therefore the greatest deposit removal. This technique is however not universally used within the water industry. The main reason for not using the "collapse-pulsing" method of backwashing is the fear of media loss over the wash weirs, especially in the case of dual-media filters with a top layer of anthracite.

Good filter design should minimise this problem however, with correctly placed and sized wash weirs and the optimum media size range. Problems with media loss have been known to arise with retro-fitted backwash systems where the combined air and water wash has been added at a later stage without due attention to the filter design. Media loss is to be avoided as the removal efficiency of the filter decreases and media can permeate through to parts of the process where sand grains can be a problem such as balance tanks which feed backwash pumps. There has been some consideration given to "enhanced backwashing techniques" such as polymer and/or metal based coagulant addition to the backwash water supply (Cranston and Amirtharajah, 1987; Francois and Van Haute, 1985; Yapijakis, 1982; Harris, 1970) but these all come with potentially serious drawbacks. Addition of coagulants to the backwash water supply can lead to the formation of floc in the under-drains which could the lead to blockage of the nozzles and potentially dangerous under-bed pressures developing during backwash. Also the correlation between the filter influent quality and the optimum dose of coagulant to add to the backwash would have to found experimentally using a pilot plant and would therefore be laborious and costly. The addition of extra coagulants would also add to the overall process treatment cost.

Part 2.16 The Filter Ripening Sequence and Filter Cycle

Previous research has indicated that the initial deterioration seen in filtered water quality is influenced by:

- The remnant backwash water remaining within the filter media at the end of the operation (Amirtharajah, 1980)
- The influent water quality (Francois and Van Haute, 1985)
- The hydraulic conditions of the filter (Suthaker *et al*., 1998)
- Filter media characteristics
- Coagulants and filter aids used
- The start-up procedure (Colton *et al.*, 1999)

It is important to consider all of the above influences on filter ripening when designing filter plants as it is crucial to achieving optimum output of potable water. It is useful to consider the

above five influences further as they are important in understanding the filtration ripening sequence. The final period of operation is not always characterised by filter breakthrough, it may be terminated at high headloss without deterioration in water quality. The filter ripening process was first researched extensively by Amirtharajah and Wetstein in 1980, and was later developed further by Cranston and Amirtharajah in 1987 where they developed the principle of the filter ripening sequence (FRS). The filter ripening sequence as detailed by Amirtharajah and Wetstein (1980) and Amburgey (2005) can be divided into five distinct stages as shown in figure 3:

1. The lag phase – clean backwash water remaining in the underdrain of the filter at the end of the backwash phase is the first water to leave the filter in forward flow. This clean water is responsible for the initial good quality filtrate.
2. Media disturbance and intra-media remnant stage – this is due to particles dislodged from the backwash process remaining within the filter pores. Also consolidation of the media may cause further particles to dislodge due to collision and abrasion between the media grains.
3. Upper filter remnant stage – this is due to backwash particle remnants leftover from the backwash remaining within the filter above the media and up to the backwash outlet pipe.
4. Influent mixing and particle stabilisation stage – this is due to mixing of the filter influent water with the backwash remnant water.
5. Dispersed remnant and media conditioning stage – newly attached particles become collectors or other particles within the filter and improve filter performance.

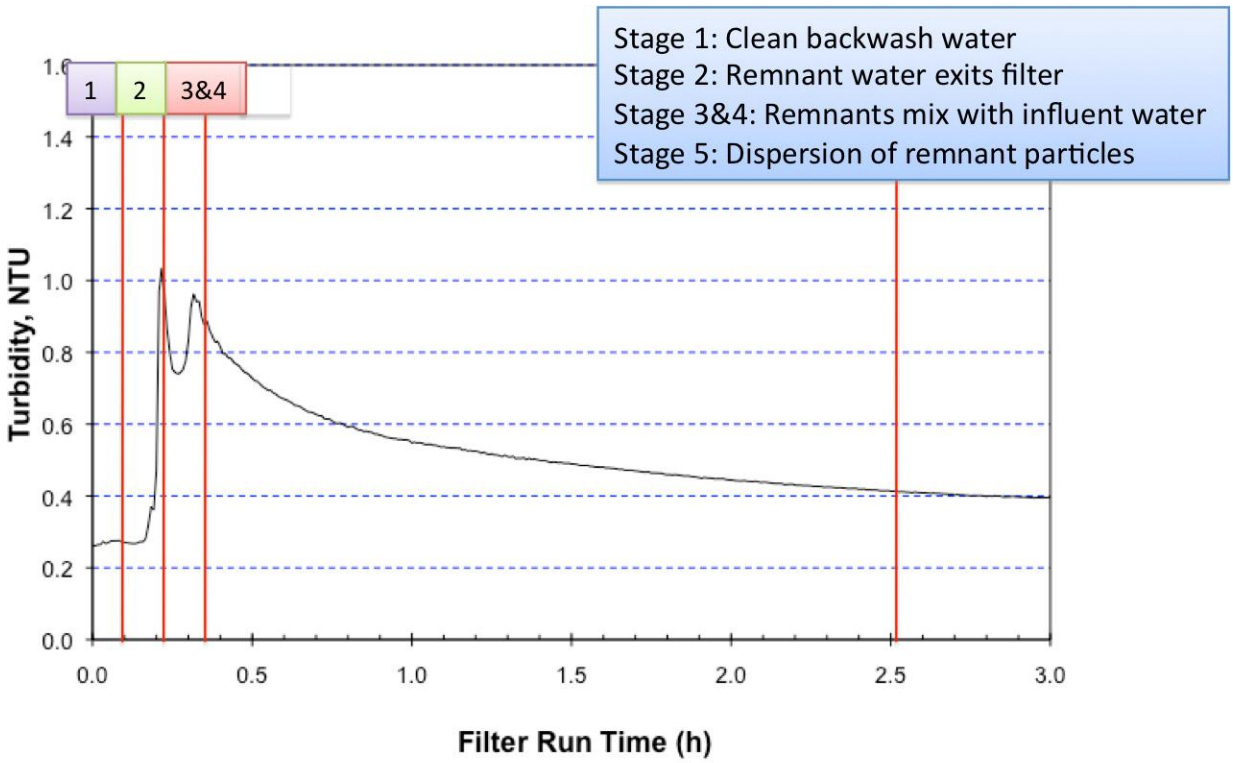


Figure 3 Graphical illustration of the stages of filter ripening (Amirtharajah and Wetstein, 1988; Amburgey, 2005)

At the start of a filter run, the filtrate quality is poor and this is known as the ripening phase. This period of ripening lasts approximately 1 hour, after which the effluent quality can be expected to be maintained at a good level for some time before deterioration (Amirtharajah, 1988). It is important to minimize the duration of the ripening period as it has been shown that the filter is highly susceptible to passing through pathogens such as *Cryptosporidium parvum* during this time (Amburgey *et al*., 2001b; Logsdon *et al*., 1981). At the end of the ripening period the filtrate quality improves to a constant level for a period of time (usually between 12- 24 hours), then the filtrate quality deteriorates rapidly and "breakthrough" occurs. Moran *et al*. (1993) conducted experiments which showed that after a certain length of time, the filter effluent quality deteriorates and this can be attributed to the process of breakthrough. It should be noted that in practice filter runs are terminated upon the basis of either breakthrough or terminal head loss, so it is possible to operate without seeing breakthrough because the system is such that the headloss build up is the limiting factor.

In some cases it has been noted that breakthrough occurs at low headloss during weak floc conditions (Robeck *et al*., 1964), it is this phenomenon which causes the operator the most problems as the filter run has to be terminated early.

Cases where filtrate quality has continued to improve after ripening without reaching terminal headloss or breakthrough have also been documented (Cleasby, 1969). There is clearly the need to improve the filter ripening process to reduce the potential for pathogens to pass through the filter and improve process efficiency. It has also been suggested that the peak turbidity is more related to the influent water (95% of the time) rather than the remnant water (Francois and Van Haute, 1987). This study also explained that the ripening period corresponded with a change in the bed pore structure. The initial turbidity breakthrough was related to the breakdown of weak hydroxide flocs within the media, caused by rapid increases in velocity gradients as particles accumulate within the bed. This would appear to differ slightly in definition from the observations of Amirtharajah and Wetstein (1980) as they attributed the peak to the backwash remnants and not the influent water. In reality, the ripening turbidity peaks are most likely to be a function of both the influent water quality and the backwash remnants dependent on the system in question. The mechanisms for breakthrough are thought to be a combination of factors, brought about by the physical changes that occur in a filter throughout a run, and or changes in the upstream quality caused by coagulant dosing malfunction or changing raw water quality. These are reduction in particle attachment efficiency and increased particle detachment. It has proved difficult to identify whether particles breaking through the filter were detached or were never properly attached in the first place. It is thought that the dynamic shear stresses within the filter bed can be responsible for particle detachment. These dynamic shear stresses can arise from natural changes to the pattern of flow within the filter bed as the pores become clogged with attached particles, and sudden changes in flow. The effect of flow changes on filter performance has been researched on pilot and full-scale treatment works by Thurston and Fitzpatrick, 2001. Their findings are summarised below:

- Flow rate changes cause an increase in particle breakthrough (as measured by particle counters and turbidity)

- The magnitude of the flow rate change corresponds to the extent of the particle breakthrough
- Flow rate changes have a more pronounced effect during the later stages of the filter run.

Flow changes during the filter run must therefore be minimised in order to achieve optimum filter performance. If the flow changes are unavoidable as in the case when a filter is taken out of service for backwashing then it is essential that the backwash interval is optimised, in order to minimize the frequency of the flow changes. In practice during periods of difficult water quality conditions it is not uncommon to see filter run times <12 hours duration and therefore frequent backwashing and flow changes are applied to the filters and water quality is not optimised.

Part 2.17 Filter Effluent Quality Monitoring Using Particle Counters and Turbidimeters

In industry, the outlet filtrate quality is usually assessed by means of online turbidimeters as they are relatively inexpensive and the regulatory requirements are expressed in terms of turbidity with respect to filter effluent quality. However for pilot plant operation, it is usually more useful to incorporate particle counters alongside turbidimeters as these are known to be more sensitive to filter effluent quality changes than turbidimeters (Beard and Tanaka, 1977). Particle counters are instruments that are capable of both counting and sizing particles in many types of process fluids. There are three modes of operation of particle counters, these are:

- Discrete sample analysis
- On-line sample analysis
- Batch/on-line sample analysis

Particle counters comprise of two main components, a sensor and a counter. The sensor mode of operation can be split into three types:

- Light obscuration

- Light scatter
- Electrical resistance principles

Particle count and size are inextricably linked with the sample flow rate through the sensor, particle concentration in the sample, and sensor resolution. It is important that these aspects are understood in order to obtain accurate and precise particle count and size measurements. Particles ranging in size from less than 0.5 μm to over 500 μm can be sized and enumerated. Other types of analysers include particle size analysers or particle size distribution analysers, these provide particle size information but not counts. Both particle size and particle number are considered important in drinking water treatment. Particle size analysers and counters measure particles using one of two basic approaches: displacement or transformation. Displacement is the basis for both light obscuration particle counters (Liebermann, 1984) and electrical resistance particle counters (Shapiro, 1988). In displacement-type particle counters the measured parameter (light or electrical current) is displaced by a particle passing through a sensing zone. The quantity of the measured parameter detected is reduced in proportion to the size of the particle.

The most frequently used particle counting technology is the light obscuration method, and many researchers have used this method to analyse filter performance. These include studies by Beard and Tanaka (1977) which showed that particle counters provide a more sensitive measure of filter effluent quality than turbidimeters. It is supposed that as turbidity and particle counting are both measures of water quality that a relationship between the two parameters is probable, however there is little consensus in the literature regarding this matter. Some researchers (Logsdon *et al*.,1981) have found that there is little direct correlation between cumulative total particle counts per ml and turbidity. The two techniques differ fundamentally, particle count measures size and number and turbidity, a one-dimensional measure of clarity. It has been shown that water samples of identical clarity can be distinguished on the basis of particle size and number; one sample may contain many small particles, while another may contain a few large particles. Turbidity measurements can't distinguish between two samples of identical clarity and different particulate composition. It is important therefore in pilot plant investigations to incorporate both measurements where possible.

Part 2.18 Literature Review Summary

The literature previously discussed provides an excellent basis upon which to expand knowledge in the area of floc physico-chemical properties further. The characterisation of NOM has progressed from the stage of very little detailed knowledge, to considerable knowledge regarding the breakdown of the NOM content in terms of the fractional components. The exact structure is changeable from one water treatment plant to another as the origin of the NOM will never be the same due to its complex biodegradation route. The techniques available at the present time for the analysis of NOM yield useful information that could enable the optimisation of NOM removal during drinking water treatment if correctly applied. The current knowledge gap; is that of natural raw water floc physico-chemical properties, and how these properties can be affected by coagulant type/dose/pH and thereby affect the ability of the water treatment process to remove the floc successfully to achieve compliant final water quality.

As detailed earlier floc properties are not easy to quantify and it has been suggested in part 1.1 that floc properties such as size/strength play an important part in filter performance, and the coagulation efficiency of NOM and its subsequent removal. It could therefore be the parameter common to coagulation/flocculation and filtration, which if optimised, could increase the overall efficiency of the NOM removal process. This needs to be proven for a natural water system, and thus provides the basis for the research. Researchers have studied the use of optical flocculation monitors such as the PDA 2000 on synthetic waters, and to some extent on real waters but the latter is lacking in quantity. The jar test is prevalent throughout the water industry as the most popular method for establishing the most suitable coagulant and dose, but this has limitations in its application to full-scale plants. This research expands on this and should provide a more comprehensive method for monitoring coagulation performance and relating measurements such as UV_{254} absorbance removal and zeta potential to dynamic flocculation parameters such as floc strength, and ultimately filter effluent quality.

Chapter 3 Experimental Methodology

Part 3.0 Jar Test Experiments

Jar tests were carried out at UCL laboratory, London using raw water sent from Albert Water Treatment Works, Halifax. This bulk volume (15 litres) of raw water was kept refrigerated at 5ºC to prevent deterioration of the sample. The experimental setup for these jar tests varied slightly from those carried out on site at Albert WTW which are detailed in the next sub-section. Jar tests and experimental work was then carried out onsite at Albert WTW using both raw and treated water. The coagulant systems and conditions investigated, and the location of the results within this thesis are as detailed in Table 4:

Coagulant or flocculant System	Location	Temperature (ºC)	Coag pH	Origin of Water	Relevant Chapter
Ferric sulphate	UCL	22	4.5	Raw water	4
polyDADMAC	UCL	22	6	Raw water	4
Zetag 64	UCL	22	6	Raw water	4
ferric sulphate and polyDADMAC	UCL	22	4.5	Raw water	4
ferric sulphate and Zetag 64	UCL	22	4.5	Raw water	4
Ferripol XL	Albert WTW Laboratory	15	3.5 4.5 6.5	Raw water	5
Ferripol XL	Albert WTW Pilot Plant	17	4.5	DA20 flocculator inlet	6
FL17	Albert WTW Laboratory	7	6.5	DAF outlet	7
AN905	Albert WTW Laboratory	7	4.5	DAF outlet	7
AN905	Albert WTW Pilot Plant	7	6.5	Pilot filter inlet	7
AH912	Albert WTW Pilot Plant and Laboratory	7	6.5	DAF outlet, Pilot filter inlet	7
FO4090	Albert WTW Laboratory	7	6.5	DAF outlet	7

Table 4 Jar test experimental matrix

The coagulation pH was set to 4.5 for the ferric sulphate systems based on the findings of Bell-Ayj *et al*. (2000) who have shown that the optimum pH for coagulation with ferric salts is below 5. Lindqvist *et al*. (2002) performed a study on water with low TOC and low ionic strength, similar to Albert WTW raw water and found that the optimum pH for coagulation with ferric salts was 4.6. The process coagulation pH at Yorkshire Water was also set to between 4.2-4.5, and so it was useful to be able to compare performance at the same operating pH. It was thought that this pH would also be suitable for the organic coagulants when used in combination with ferric sulphate as the manufacturers' recommended an optimum pH range of between pH 4-6. Research has also shown that pH appears to have a less critical effect on the mode of operation of organic coagulants compared to hydrolysing metal salts over the range used in these experiments (Gregory and Kam, 1999). The jar tests were carried out at the raw water pH of 6 when using polyDADMAC and Zetag 64.

Part 3.1 Jar Test Methodology

Jar tests using the same method as Gregory and Yukselen (2004) using the PDA 2000 formed a major part of the research work, and there were some differences in the equipment and methods used between the tests carried out at UCL and those carried out onsite. The methods used for each test are detailed in the following sections and illustrated in figure 4.

Part 3.1.0 Jar Test Method at UCL Laboratory using the PDA 2000

The apparatus used in the experiments in Chapter 5 was as follows:

- 300 ml square beaker.
- Electric stirrer capable of stirring speeds 30-400 rpm.
- Camspec UV/Visible spectrophotometer.
- Photometric Dispersion Analyser (PDA 2000, Rank Brothers Ltd., UK) complete with Pico-log recording software package, and a computer.
- Peristaltic pump set to 1.8 ml/min situated on outlet of PDA 2000.
- 1mm internal diameter, clear tubing.
- Cranwell Universal pH 950 pH meter (suitable for low conductivity water).
- 1litre volumetric flask.

- 1000µl Pipette.
- 0.45µm sterile syringe filters and syringe

The jar test method used for the UCL based tests was as follows:

1. Stock solutions of coagulant were made up using analytical grade weighing scales to measure 1 g of coagulant (as active component), and dissolved into 1 litre of deionised (DI) water in a volumetric flask to make a 1g/l solution. Zetag 64 and polyDADMAC were available in liquid form and required 1 hour of magnetic stirring prior to use to ensure complete dissolution as per the manufacturers' instructions.
2. Decide upon the coagulant dose range to be investigated.
3. Determine the acid/alkali dose required to maintain a coagulation pH of 4.5 for ferric sulphate dose range chosen in stage 2. The pH not adjusted with polymeric additives. The coagulation pH and temperature was monitored using a low conductivity pH probe inserted into the jar.
4. Measure the UV_{254} absorbance of the raw water. A 1cm quartz cell was used in the spectrophotometer. The spectrophotometer used was a Camspec UV/Visible spectrophotometer.
5. The pH correction was carried out during the initial rapid mix period at 400 rpm for 10 seconds. The pH was monitored after the addition to check the result was within range 4.5-4.6.
6. The PDA 2000 was connected to the jar test equipment by inserting the peristaltic pump tubing into the jar to allow flow through from the jar test, through the PDA 2000 and back into the jar. The Pico-log recording software was started at this time to ensure the baseline readings were obtained before the coagulant was added.
7. Coagulant was then added during the 2^{nd} rapid mix period at 400 rpm for 10 seconds
8. The stirrer was then turned down to 50 rpm for 30 minutes to simulate flocculation.
9. The stirrer was then turned off and the sample was left to settle for 30 mins and the settled UV_{254} absorbance was measured after passing through a 0.45 um membrane to remove particulate.
10. Repeat stages 4-9 three times for the purposes of reproducibility.

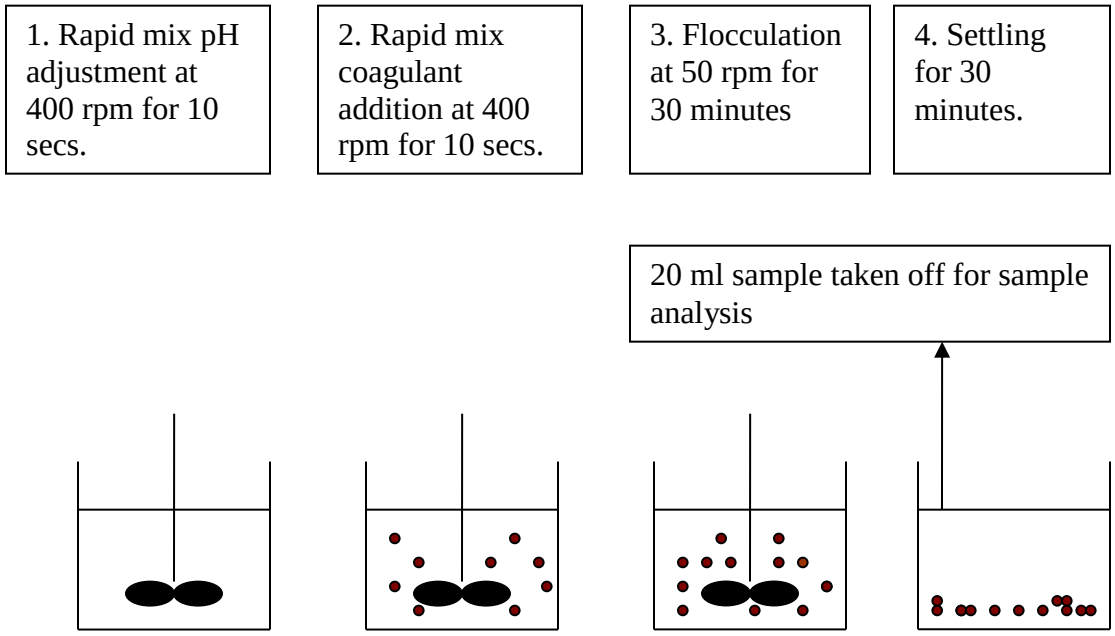


Figure 4 – The four stages of the conventional jar test for determining optimum coagulant dose

Part 3.1.1 Breakage Jar Test Procedure

The breakage test was carried out using a similar method as Gregory and Yukselen (2004) to determine the dynamic flocculation parameters of FI_{break}, FI_{ref}, FI_{max} and R_{FI}. The procedure used was as described below and illustrated in figure 5:

1. Follow steps 1-8 as described in part 3.1.0
2. After 15 minutes, increase the stirring speed from 50 rpm to 400 rpm for 30 seconds
3. Return the stirring speed back to 50 rpm for the remaining 30 minutes
4. Follow steps 9-10 as described in part 3.1.0

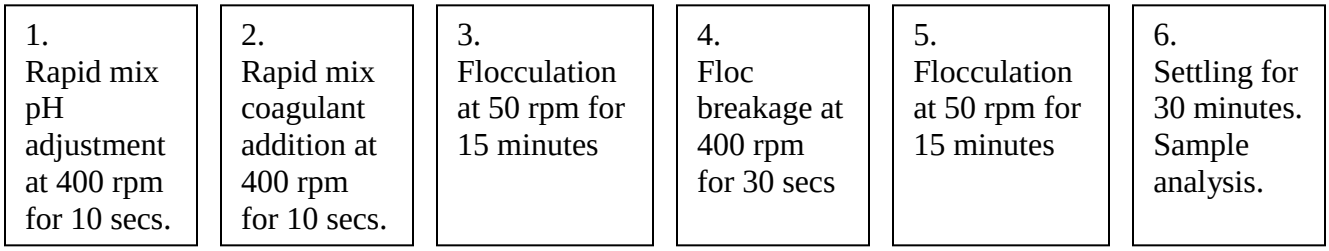


Figure 5 – Stages in the breakage jar test using the PDA 2000

Part 3.1.2 Onsite Jar Test Method at Albert WTW Laboratory using Raw Water

The apparatus used for the experiments in Chapter 5 was as follows:

- Aztec jar test unit with 5 stirrers, variable stirrer speed from 10-400 rpm. There was a flotation option but this was dysfunctional and not used.
- 1 litre borosilicate volumetric glass beakers
- Oakton series 610 low conductivity pH probe
- Camspec UV/Visible spectrophotometer with a 3cm quartz measuring cell
- Hach bench-top turbidimeter
- Photometric Dispersion Analyser (PDA 2000, Rank Brothers Ltd., UK) complete with Pico-log recording software package, and a laptop.
- Peristaltic pump set to 1.8 ml/min situated on outlet of PDA 2000.
- 1mm internal diameter, clear tubing.
- 1litre volumetric flask.
- 1000µl Pipette.
- 0.45µm sterile syringe filters and syringe
- Malvern Instruments Zetasizer 2000
- TOC analyser for measuring DOC. Samples filtered through the 0.45µm membrane filters and analysed with a TOC analyser, is a suitable method for measuring DOC.*

*This analysis was carried out by Yorkshire Water's UKAS accredited laboratories.

The same jar test methodology was used as described earlier, and illustrated in figures 3 and 4.

Part 3.1.3 Onsite Jar Test Method at Albert WTW using Treated Water

The same procedure was followed as detailed in part 3.1.0 for the tests using treated water but there were some subtle differences in the procedure for obtaining the treated water sample dependant on the water treatment stage, and these are outlined as follows:

- Breakage jar tests carried out alongside the DA20 pilot plant were designed to test whether water taken from the DA20 flocculator inlet could be used to derive dynamic flocculation data from and relate to filter performance. These can be found in Chapter 6. The samples were obtained by tilting the 1 litre jar sideways into the flocculator inlet and filling to the 800 ml mark. The sample was then placed in the jar test stirrer and then the breakage jar test procedure as illustrated in figure 5 was followed. The initial stage of rapid mix was omitted as the water was already mixed and dosed on the pilot plant.

- Breakage jar tests were carried out using Albert WTW DAF outlet water in order to establish which flocculants would be suitable for increasing floc strength. These can be found in Chapter 7, and the water from these experiments was taken directly from the DAF outlet channel downstream of the pre-filtration lime dose. This sample was obtained by lowering the jar into the filter inlet channel and filling slowly to minimise floc breakage. The sample was then placed in the jar test stirrer and then the breakage jar test procedure as illustrated in figure 5 was followed. The initial stage of rapid mix was omitted.

- Breakage jar tests were also carried out using Albert WTW DAF outlet water which was dosed with flocculant in the pilot filter plant mixing tank. These can be found in Chapter 7. The samples for these jar tests were obtained by lowering the 1 litre glass jar sideways into the mixing tank and filling to the 800 ml mark. The sample was then placed in the jar test stirrer and then the breakage jar test procedure as illustrated in figure 5 was followed. The initial stage of rapid mix was omitted.

Part 3.2 Chemicals used in Jar tests and Pilot Filtration Experiments

The chemicals used in the experiments can be split into three sections according to their purpose:

1. Primary Coagulants – ferric sulphate (Sigma Aldrich), Ferripol XL (EA West), polyDADMAC (Ciba Speciality Chemicals), Zetag 64 (Ciba Speciality Chemicals).
2. Acid/bases – Sodium Hydroxide (Sigma Aldrich), Hydrochloric Acid (Sigma Aldrich), Kalik (Buxton Lime).
3. Flocculants – AN905 anionic polyacrylamide (SNF Floerger), AH912 non-ionic polyacrylamide (SNF Floerger), FO4190 cationic polyacrylamide (SNF Floerger), FL17 cationic polyamine (SNF Floerger).

A selection of organic, and inorganic coagulants were used in the primary coagulation jar tests with the intention being to correlate floc properties, coagulant type and removal efficiency, and identify systems with improved floc properties and good removal efficiencies. Organic coagulants are known for forming stronger more reversible floc compared to hydrolysing metal salts (Gregory and Yukselen, 2002) which is why they were chosen as a comparison with ferric sulphate. The properties of the organic polymeric coagulants polyDADMAC and Zetag 64 are summarised below:

- Magnafloc 1697 - (poly(diallyldimethylammonium chloride) or polyDADMAC) MW approximately 50,000 Daltons and charge density of around 6 meq/g (Gregory and Yukselen, 2002)
- Zetag 64 – Copolymer of acrylamide and a cationic monomer (40 mole% cationic), molecular weight several million Daltons (Gregory and Yukselen, 2002).

Part 3.3 Analysis of dynamic flocculation curves

The breakage jar tests were carried out alongside conventional jar tests, to allow for direct comparison of the results. All jar tests were carried out 4 times to check for reproducibility, and quantify the experimental error. The PDA 2000 monitor produced an electrical current that was proportional to the size of the particle passing through the light beam (Gregory and Nelson, 1986), this signal was sent to a PC via an interface system, and the end result was production of dynamic flocculation curves that were recordable and comparable between jar test systems. This system is a vast improvement on subjective visual observations, or use of the floc size charts. Interpretation of the dynamic flocculation curves was possible on many levels as there are several important parameters that can be derived from the curves that are of use in evaluating the dynamic flocculation characteristics of the system. Figure 6 shows an example of a typical dynamic flocculation curve obtained from a ferric system coagulated at pH 4.5 during a conventional jar test using Albert WTW raw water.

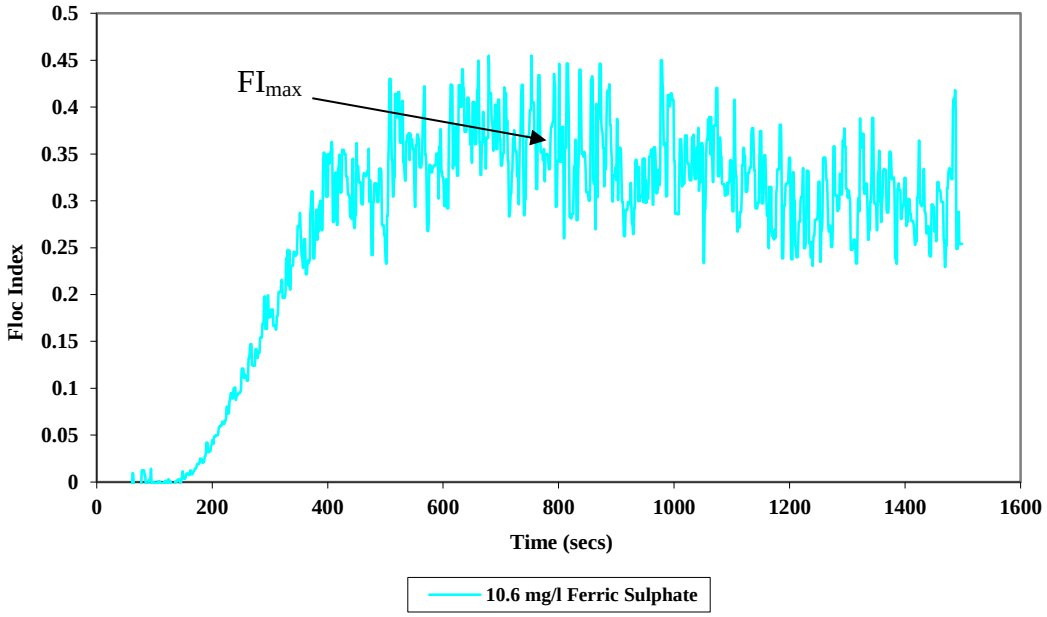


Figure 6 Example of flocculation curve obtained using the PDA and 10.6 mg/l ferric sulphate as Fe^{3+} at pH 4.5

There are important parameters that can be derived from the flocculation curves and these are the maximum floc index value reached (FI_{max}), and the rate of increase in floc index up to the point FI_{max} which has been shown by Gregory and Kam (2001) to be indicative of the performance of

the coagulation process as a whole. The rate of increase of FI with time is referred to in this work as R_{FI}, and this is representative of the speed of particle de-stabilisation, and can be related to coagulation performance. The parameters shown on the flocculation curve are all useful comparators between jar test systems and can provide more information about the dynamic flocculation process than conventional removal parameters such as UV_{254} absorbance and turbidity. Figure 7 shows an example of a typical dynamic flocculation curve obtained from a breakage jar test carried out using a ferric/NOM system coagulated at pH 4.5. The graph in figure 7 shows the typical shape of a flocculation curve obtained from the breakage tests detailed in part 3.1.1. In this case, it is useful to split the flocculation curves into 3 stages. These three stages can be described as:

1. Floc growth stage to a steady-state floc index value. (FI_{max})
2. Floc breakage to a minimum floc index value (not the min floc index value present on un-coagulated solution). (FI_{break})
3. Floc re-growth to 2nd steady-state floc index value after breakage. (FI_{ref})

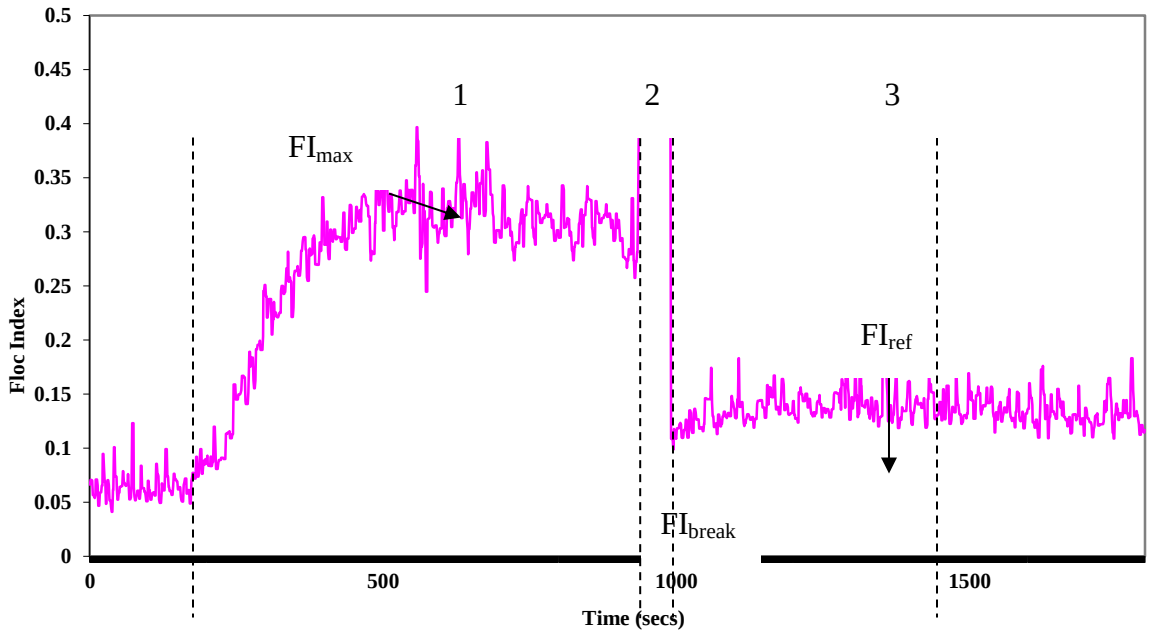


Figure 7 Example of floc breakage and reformation curves using 10.8 mg/l ferric sulphate as Fe^{3+} at pH 4.5

Increases in floc index value at the onset of the rapid mixing period in this test were due to the formation of air bubbles which pass through the PDA and disrupt the reading, and do not represent sudden increases in floc size, and therefore can be ignored. This was remedied in subsequent jar tests by altering the sample take-off position from above the vortex to underneath the vortex created by the impeller. The stages described above are all important in understanding the system floc physical properties. As before, the value of FI_{max} is indicative of the maximum floc size. The use of the moving average function in Excel was also used when displaying more than 1 system flocculation curve on the same axis for ease of viewing the separate systems clearly. The moving average was set to 15 samples in these cases. Figure 8 shows the floc growth, breakage and reformation as modelled by the Sigmoid function.

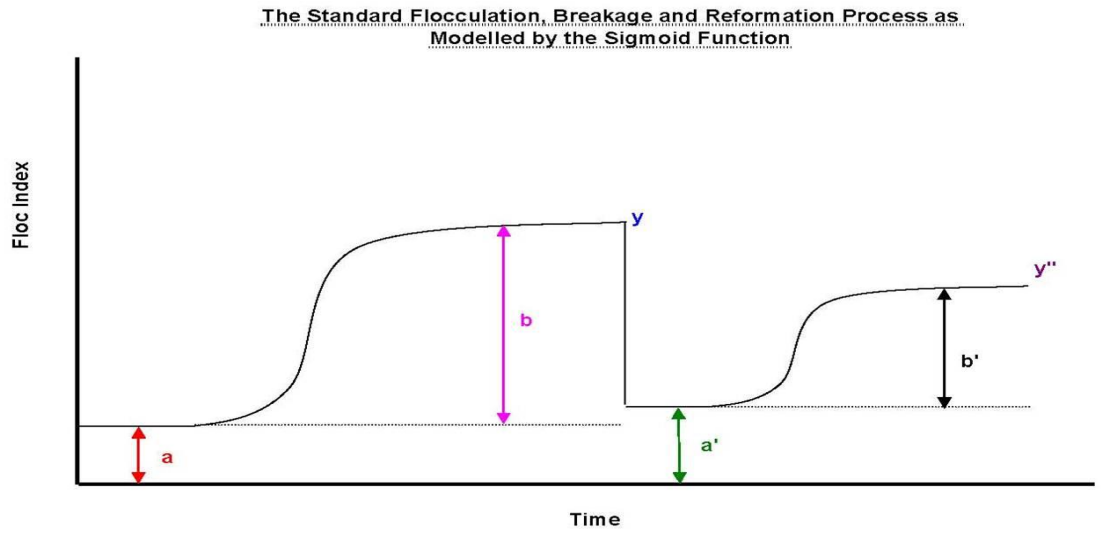


Figure 8 Modelling the flocculation index curves by the Sigmoid Function

The constants shown on figure 8 are explained below:

a – the initial displacement of the flocculation index from the x axis – representative of the system "noise"
a' - the flocculation index reading after the breakage period (FI_{break})
b - the maximum flocculation index reading before the breakage regime (FI_{max})
b' - the flocculation index at the end of the breakage test (FI_{ref})
y - b + a
y' - b' + a'

The ratio of the $(FI_{ref}-FI_{break})/(FI_{max}-FI_{break})$ can be better described as the floc reformation factor (F_{ref}), which can be calculated by modelling the flocculation curves to the Sigmoid function. This enables accurate calculation of the two parameters FI_{ref} and FI_{max}. The ratio F_{ref} describes the degree of floc reformation after breakage in comparison to the steady-state floc size before breakage. The floc strength factor (F_{brk}) is also important, as the degree of resistance of floc to high shear is an indicator of strength, and this can be expressed as FI_{max}/FI_{break}. The values of these ratios can be determined graphically by qualitative analysis of the curves, or numerically by solving the Sigmoid function for particular values of time (t). The benefit of using the parameters derived from a fit to the Sigmoid function is that any noise in the data can be smoothed. The data from the flocculation curves was transported into a curve-fitting software tool called Table-Curve^{TM} which calculated the values of the constants a, b and c (maximum rate of increase of flocculation index with time) for the floc growth curve and the floc re-growth curves thereby allowing the floc reversibility, strength factor and maximum flocculation rate to be expressed in numerical form. The flocculation curves generated from the breakage jar tests were split into two curves, the initial floc growth to FI_{max} and the subsequent re-growth from FI_{break} to FI_{ref}. All of the parameters discussed above have been used to evaluate the performance of different coagulant systems, as well as the more conventional parameters such as UV_{254} absorbance removal and turbidity. Zeta potential was also used for all the tests carried out onsite at Albert WTW by injecting samples of the water into the Zetasizer 2000.

Part 3.4 Analysing the flocculation data using Table-Curve^{TM}

The software package was used to express the FI data in the form of the Sigmoid function. The first stage in the curve-fitting process was to assess how well the data fitted the Sigmoid function, and this was evaluated by the regression coefficient as calculated by the software package. It was decided that a value of regression coefficient of > 0.8 implied that the data was a suitable fit to the Sigmoid function and the numerical analysis would be useful and more accurate than qualitative analysis of the graphs. The values of the constants a,b and c were then derived. In some cases the data didn't fit the Sigmoid function well, and interpretation of the data was left to graphical means for calculation on F_{brk} and F_{ref} .

In the case of the breakage tests, the data was split into two sections (initial growth, and re-growth after breakage) and analysed separately. Example 1 shows the results generated from Table-curve™ using the PDA data from a breakage test involving 12 mg/l Ferripol XL as Fe^{3+} at coagulation pH of 3.5.

Example 1 – Applying the curve-fitting package to data obtained from a breakage jar test

Data taken from a breakage jar test carried out using 12 mg/l Ferripol XL as Fe^{3+} at pH 3.5 is illustrated in this example. The following procedure was carried out:

1. Import the data into Table-curve™ (This is time in seconds on the x axis, and FI on the y axis).
2. Initiate the curve-fitting process.
3. Select the Sigmoid Function.
4. Evaluate the suitability of the curve-fit via the regression coefficient r, if $r>0.8$ then proceed to 5. If $r<0.8$ then terminate Table-curve™ and analyse trends graphically.
5. Generate a spreadsheet of the data with the curve-fitting trends, and the table of parameters.
6. Analyse parameters and compare coagulation systems.

The graph in figure 9 shows that the data fits the Sigmoid function very well at most points along the curve with just a slight deviation along the early part of the curve. This was most likely to be due to the fact that the raw water wasn't filtered before the jar tests and there would have been a baseline level of particles present to account for the reason that the FI value at the beginning of the breakage tests was not zero. The important parameters taken from Table-curve™ are shown below in table 5. The rate of change of FI with time is not constant and therefore when comparing systems it is important to compare the same reference point, and for this reason it is logical to compare the maximum rate of change in FI, ie: dFI/dt at its maxima. This is also the point reported by Gregory and Kam (2001) to be very sensitive to the performance of the coagulant system. This is referred to in this work as R_{FI}.

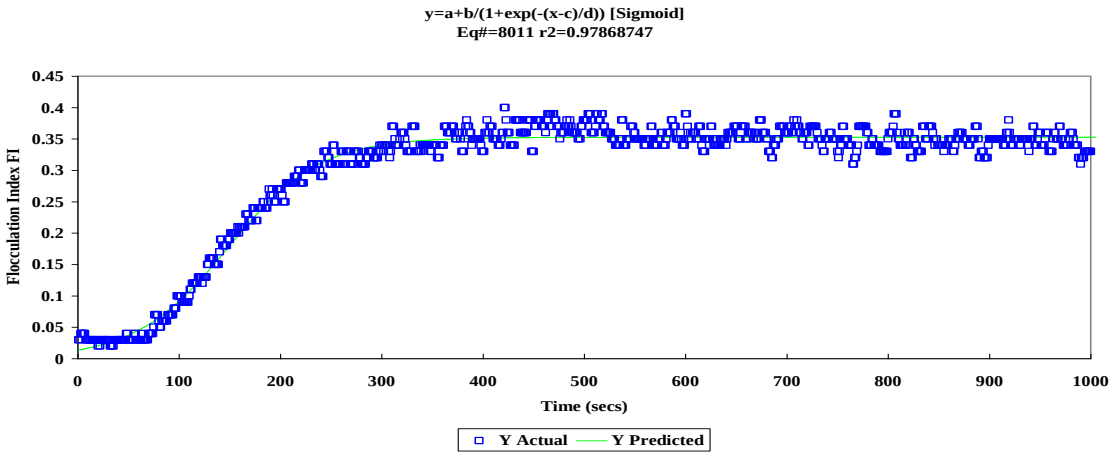


Figure 9 Curve-fitting example using 12mg/l Ferripol XL at pH 3.5, floc growth curve

The second part of the curve corresponding to the re-growth phase after breakage is shown in figure 10. The curve in figure 10 shows a flatter Sigmoid shape, with a regression coefficient of 0.85 which was still within the reasonable range. The fact that the regression coefficient is less for the re-growth curve is most probably due to the fact that the floc doesn't break down completely therefore there isn't a very long period of baseline readings normally seen in the early parts of the Sigmoid curve shape.

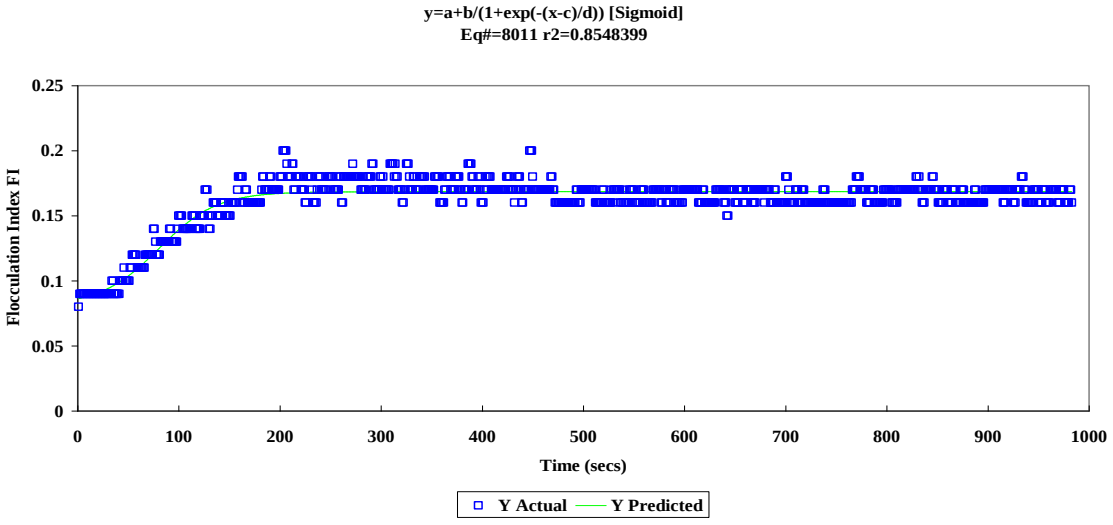


Figure 10 Curve-fitting example using 12 mg/l Ferripol XL as Fe^{3+} at pH 3.5, floc re-growth curve

Table 5 shows some of the parameters obtained from Table-curve^{TM}, the constants are as explained earlier. The dynamic flocculation parameters can therefore be consistently calculated for each system and compared along with the conventional UV_{254} absorbance, and turbidity measurements. In the case of the data not fitting the Sigmoid curve, it was likely that the flocculation was poor or the data noisy.

System	a	b	c *	dy/dx MAX
12 mg/l Ferripol, pH 3.5 (floc growth)	0.000482	0.35	147.8	0.0019
12 mg/l Ferripol, pH 3.5 (floc re-growth)	0.081	0.09	80.2	0.00076

Table 5 Flocculation curve parameters using 12 mg/l Ferripol XL at pH 3.5, * c – maximum rate of increase in flocculation index with time or R_{FI}

Part 3.5 Summary of jar test parameters used to evaluate coagulation performance

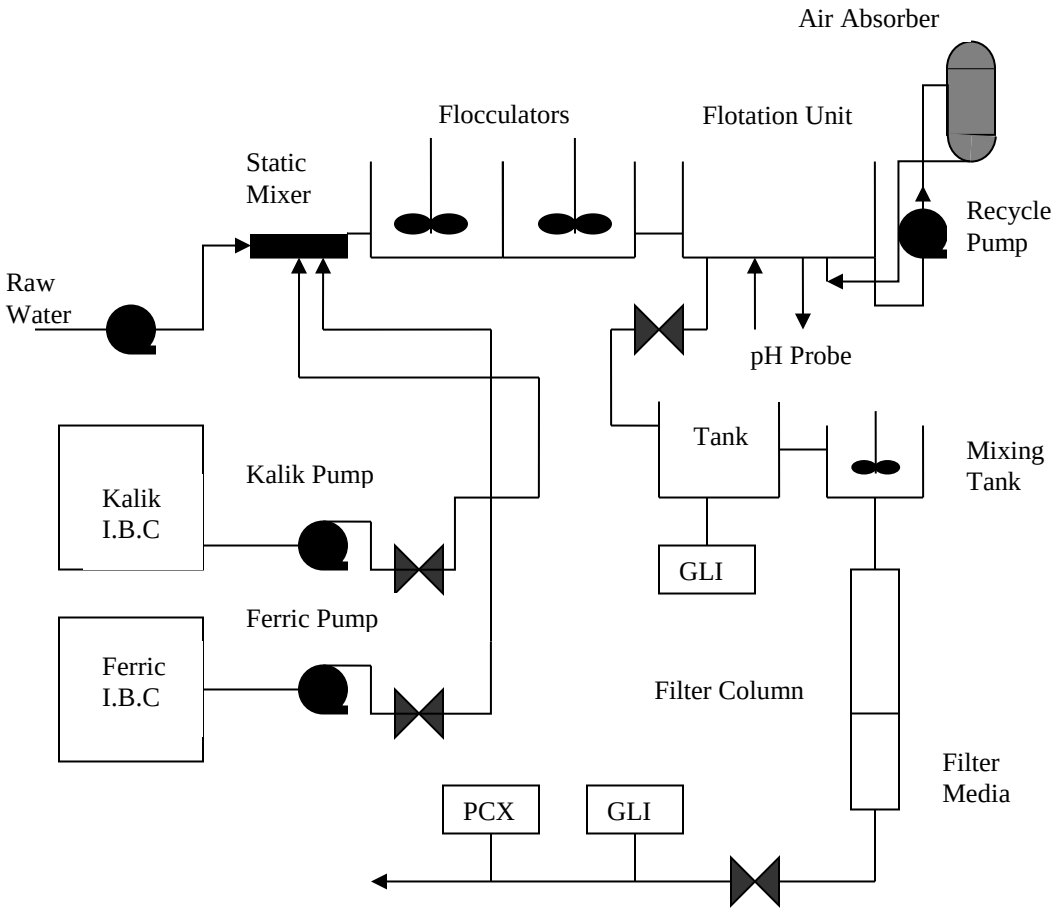
There are many important parameters that can be measured when carrying out a coagulant dose optimisation jar test, and each parameter has a particular purpose, however it is useful to take a broad approach when evaluating jar test performance as it's known that the jar test by itself isn't a particularly accurate process performance indicator. Table 6 summarises the jar test parameters used in this project and the reasons for using these measures.

Parameter	Reason for measuring	Limitations
UV_{254} (abs/m)	Indicates how well optimised the coagulant dose is for NOM removal	Reading often different for the same sample.
Turbidity (NTU)	Settled turbidity gives some idea of how well the floc floats or settles.	Difficult to interpret accurately as it's not an accurate measure like concentration.
Zeta Potential (mV)	Indicates the general success of the coagulant dose with regard to charge neutralization of the NOM	The optimum range varies greatly between systems and can be quite a large operating range. Difficult to relate directly to floc physical properties.
Dynamic Floc Measurements	Indicates the floc size, strength and the speed at which coagulation/flocculation occurs and the degree of reversibility of the floc formation when exposed to shear	The full use of dynamic floc characteristics has yet to be determined. Initial limitations are that there is no easy way of correlating mixing conditions in a jar/vessel to those on the main plant. Correlations between dynamic floc characteristics and NOM removal also not known as yet

Table 6 Summary of parameters recorded during jar test experiments (zeta potential and turbidity not available during chapter 4 experiments)

Part 3.6 DA20 Pilot Plant Equipment and Methodology

Figure 11 shows the design of the pilot-scale treatment plant created from connecting the DA20 pilot plant to the filter column. Photographs are included in figures 12 to 15. Details of the operating procedure can be found in appendix 1. Raw water was pumped from the plant inlet channel via a submersible pump into the static mixer on the DA20 unit. Coagulant and kalik suspension was added into the static mixer, and the resulting liquor was fed to flocculators. The liquor containing floc then passed into a DAF unit where the floc was removed hourly via a scraper device. Clean treated water was then fed by gravity into the pilot filter header tank, which in turn fed the mixing tank and pilot filter column. The flow through the DA20 pilot plant was set to 15 m^3/hr which is within the design maximum flow of 20 m^3/hr , and coagulation pH was manually controlled to achieve a setpoint of 4.5.



Key

PCX – MetOne Particle Counter

GLI- Great Lakes Instruments Turbidimeter

Figure 11 Schematic showing the DA20 pilot filter plant and instrumentation

Ferripol XL Dose as Fe^{3+} (mg/l)	Coagulation pH	Number of Filter Runs	Number of Breakage Jar tests (per run)
6	4.5-4.6	3	5
7	4.5-4.6	3	5
9	4.5-4.6	3	5 (no data from run 3 due to fault with PDA)
11	4.5-4.6	2*	5

Table 7 DA20 Ferripol XL dosing trial experiment matrix

*The third run could not be completed as the scraper mechanism had broken, and the plant was needed elsewhere.

The coagulant dose was calculated from the pump flowrate, and the kalik dose was manually adjusted to give the desired pH for the respective Ferripol XL dose for each run. The pH was measured via a Rosemount pH probe, the output of which was displayed continuously. The floted water was diverted to waste during the start-up period of operation until the turbidity, pH and UV_{254} absorbance reached a steady-state level, whereupon the feed was opened to the pilot filter. During the initial commissioning runs the kalik suspension proved difficult to pump with a diaphragm pump, and therefore the coagulation pH was hard to maintain at a constant value as the pump and lines continually blocked with kalik solids. The system was then modified so that the kalik suspension was diluted in a stirred tank, and the resulting solution was easy to pump via a peristaltic pump and coagulation pH control was improved.

The saturator pressure was kept at 6.5 bar by maintaining the level of recycle water at a pre-determined level found by trial and error, as the automated system was broken. As the saturator pressure and de-sludge scraper could not be controlled automatically, the DA20 filter runs were restricted to 5-6 hours of steady-state operation. Samples of the coagulated mix were taken from the flocculator inlet and breakage jar tests were performed on these samples 5 times during each run in order to generate information regarding the floc properties, and they how they were affected by the coagulant dose changes.

Table 8 shows the method and frequency of data measurement during each run.

Ferripol XL Dose as Fe^{3+} (mg/l) ***Fe:DOC Ratio***	6 ***0.7***	7 ***0.8***	9 ***1***	11 ***1.2***
Zeta Potential (mV)	6 hourly measurements per run	6 hourly measurements per run	6 hourly measurements per run	6 hourly measurements per run
Floted Turbidity (NTU)	6 hourly measurements per run	6 hourly measurements per run	6 hourly measurements per run	Online GLI monitor
Filtered Turbidity (NTU)	Online GLI monitor	Online GLI monitor	Online GLI monitor	Online GLI monitor
Filtered Particle Counts (counts/ml)	Online MetOne Particle Counter	Online MetOne Particle Counter	Online MetOne Particle Counter	Online MetOne Particle Counter
Coagulation pH	Online Rosemount pH probe – not logging recorded hourly	Online Rosemount pH probe– not logging recorded hourly	Online Rosemount pH probe– not logging recorded hourly	Online Rosemount pH probe– not logging recorded hourly
Filtered DOC (mg/l)	6 hourly measurements per run	6 hourly measurements per run	6 hourly measurements per run	6 hourly measurements per run
Filtered UV_{254} absorbance (abs/m)	6 hourly measurements per run	6 hourly measurements per run	6 hourly measurements per run	6 hourly measurements per run
Filtration Flowrate (l/min)	Online ABB Magflow	Online ABB Magflow	Online ABB Magflow	Online ABB Magflow
Headloss (m)	Not measured online, pressure gauges used	Not measured online, pressure gauges used	Online Endress and Hauser differential pressure monitor	Online Endress and Hauser differential pressure monitor
Dynamic Flocculation measurements	5 sets from each run. 15 data sets in total.	5 sets from each run. 15 data sets in total.	5 sets from run 1 and run 2. 10 data sets in total.	5 sets from each run. 10 data sets in total.

Table 8 Data measurement strategy DA20 Ferripol XL dosing trial

Figure 12 DA20 Pilot Plant

Figure 12 illustrates the DA20 pilot plant, shown in blue on the left. The kalik tank and bund is shown on the bottom right. The static mixer with Ferripol XL and lime dose is shown on the bottom left.

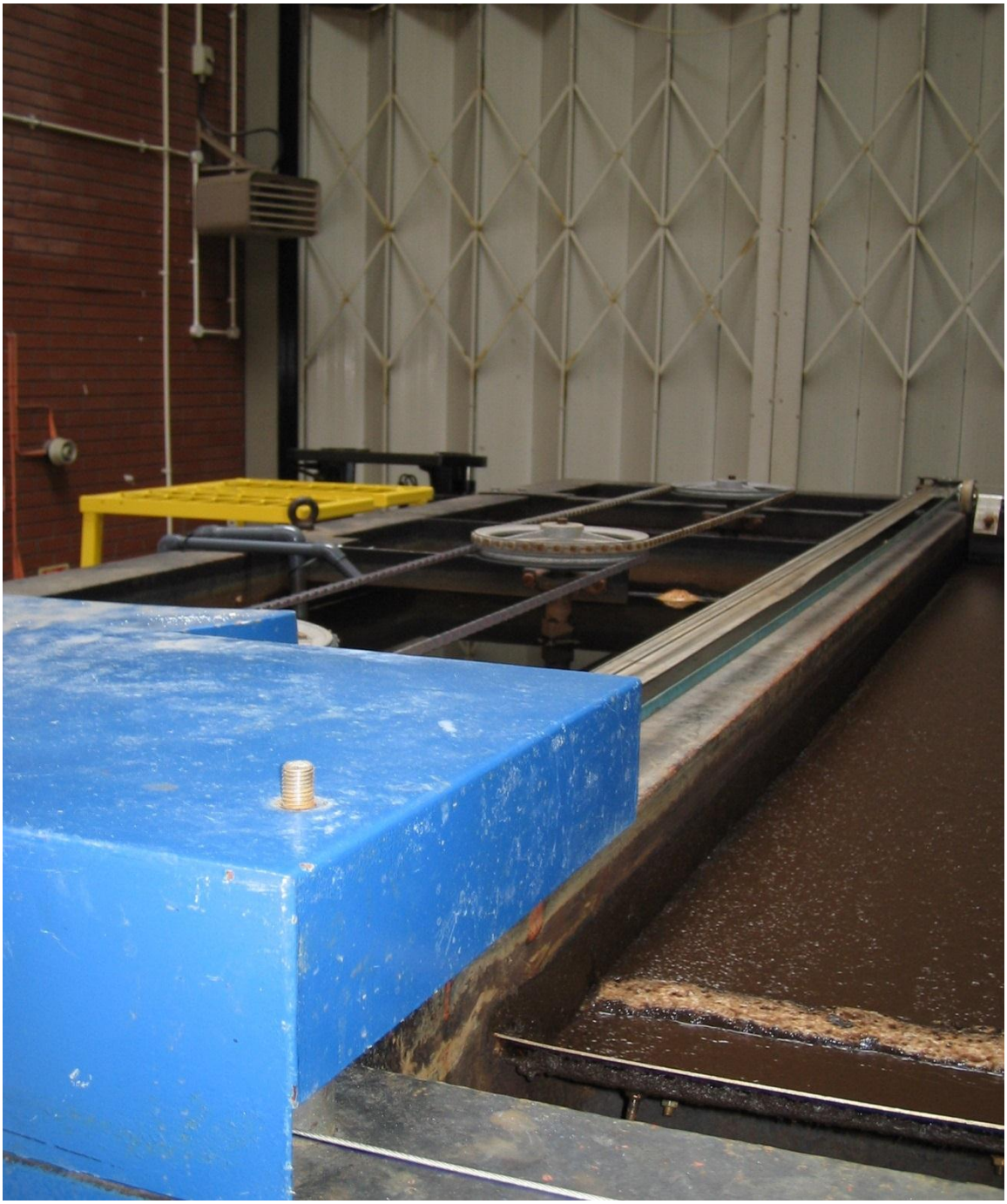


Figure 13 DA20 Pilot plant showing flocculators and floc blanket

Figure 13 shows the top view of the DA20 plant, with the 3 stage flocculators shown on the left and the DAF unit on the right with sludge blanket present. The scraper unit is shown at the far end of the picture.

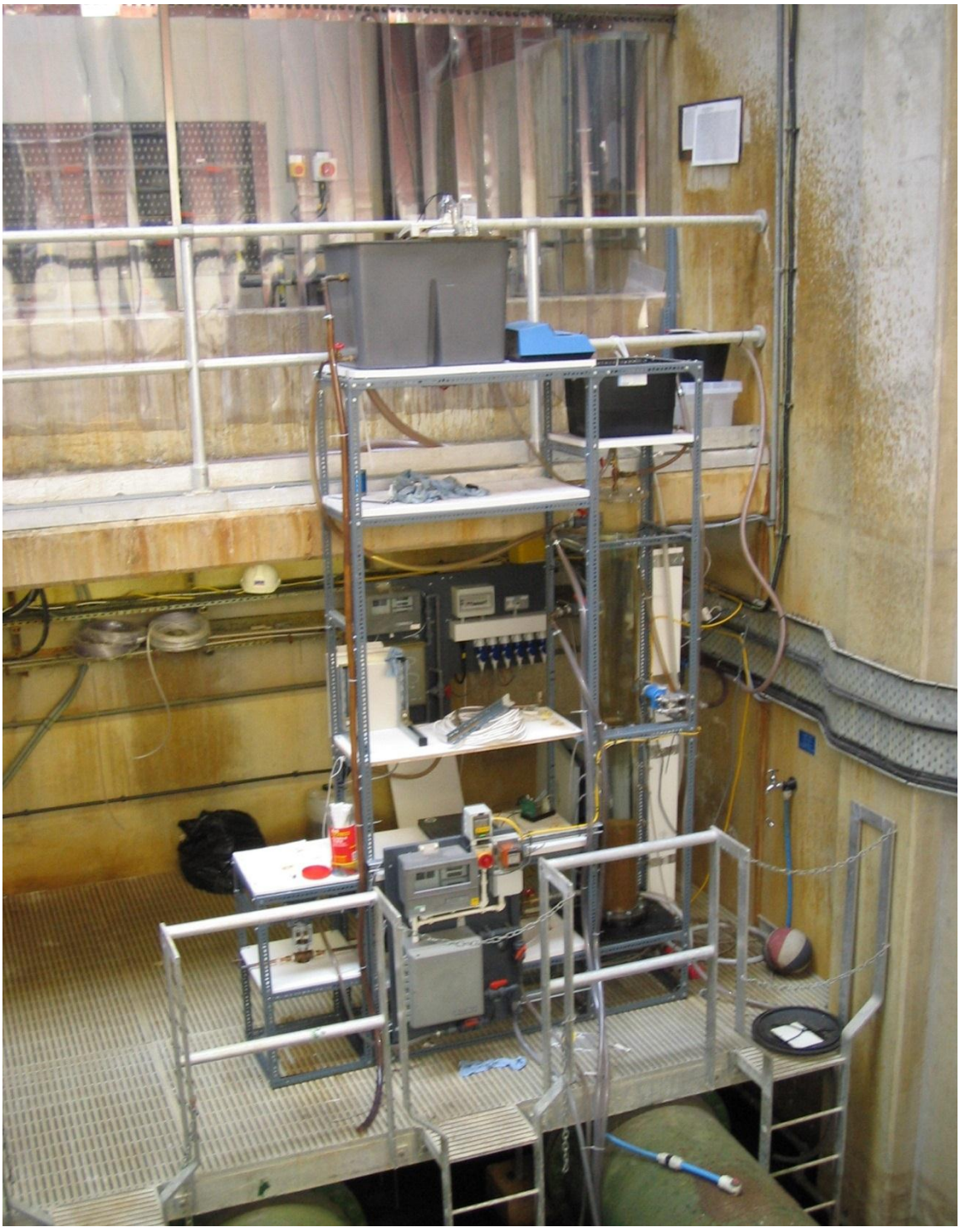


Figure 14 Pilot Plant Filtration Column

Figure 14 shows the pilot filter column from the top, the grey tank shown is the header tank and the black tank is the mixing tank.

Figure 15 Pilot Plant Filtration Column

Figure 15 shows a close-up of the pilot filter column and instrumentation. The Magflow flowmeter is shown on the bottom right, and the particle counter on the bottom left.

Part 3.7 – Filtration Experimental Equipment and Methodology

Figure 16 shows the experimental apparatus used for the filtration experiments using polymeric additives, the results from which can be found in Chapter 7. The pilot filter rig was fed directly from Albert WTW DAF outlet channel. The feed water was pumped through a mono pump into an overflow tank, the overflow tank fed water into a mixing tank situated on top of the filter column. The mixing tank was kept at a constant level via a ball valve level device. The mixing tank then fed the top of the filter column. The flow through the column was controlled by an outlet globe valve, and measured by an ABB Magflow flowmeter. The filter was designed to operate in declining flow mode with the ability to operate in constant flow mode if a flow control valve and controller unit were to be added. Filter performance was assessed continuously by monitoring the filtered turbidity, flowrate, particle counts and headloss throughout the filter run via a data logging interface system. Analogue outputs were taken from the turbidity monitor, flowmeter and differential pressure transmitter; these were connected to a Pico-Log data logger that was in turn connected to a laptop. The use of Pico-Log software enabled the data to be displayed in a meaningful real-time format. A GLI turbidity monitor was installed on the inlet to the overflow tank in order that the inlet turbidity could be monitored and recorded. Samples were taken of the:

- Raw water
- Dosed raw water (raw water after lime and Ferripol XL addition)
- Floted water (water exiting DAF units before pH correction)
- Pilot filter feed water (pH corrected water exiting DAF units)

and analysed hourly for zeta potential using a Malvern Instruments Zetasizer 2000.The start-up, shutdown and backwash procedures can be found in the appendix 1.

Part 3.7.0 Filtration Experiments Matrix

The filtration experiments carried out are listed in table 9 for clarity: 4 control filter runs were carried out during the filter runs using DAF outlet water but the data from these 4 runs was lost due to a corrupted disk.

Feed water origin	Run no.	pH	Ferripol XL dose as Fe^{3+} (mg/l)	Flocculant Dose (mg/l)	Flow Change Applied (Y/N)	Relevant Chapter
DA20	3	4.5	6	0	N	6
DA20	3	4.5	7	0	N	6
DA20	3	4.5	9	0	N	6
DA20	2	4.5	11	0	N	6
Albert WTW DAF	1	4.5	15	0.005 AH912	N	7
Albert WTW DAF	1	4.5	15	0.01 AH912	N	7
Albert WTW DAF	1	4.5	15	0.02 AH912	N	7
Albert WTW DAF	1	4.5	15	0.05 AH912	N	7
Albert WTW DAF	1	4.5	13.5	0.005 AN905	N	7
Albert WTW DAF	1	4.5	13.5	0.01 AN905	N	7
Albert WTW DAF	1	4.5	14	0.02 AN905	N	7
Albert WTW DAF	1	4.5	14	0.05 AN905	N	7
Albert WTW DAF	2	4.5	15	0.05 AH912	Y	7

Table 9 Filtration run experimental matrix

Part 3.8 Design of the Pilot Filtration Plant

The filter rig consisted of the following apparatus:

1. Inlet mono-pump.
2. Header tank, (70l)
3. Mixing tank (30l)
4. Perspex filter column containing 0.45m sand.
5. Polymer dosing unit (5l glass bottle, magnetic stirrer, peristaltic pump and tubing).
6. 1.5" reinforced hose, isolations valves and instrumentation as described previously.

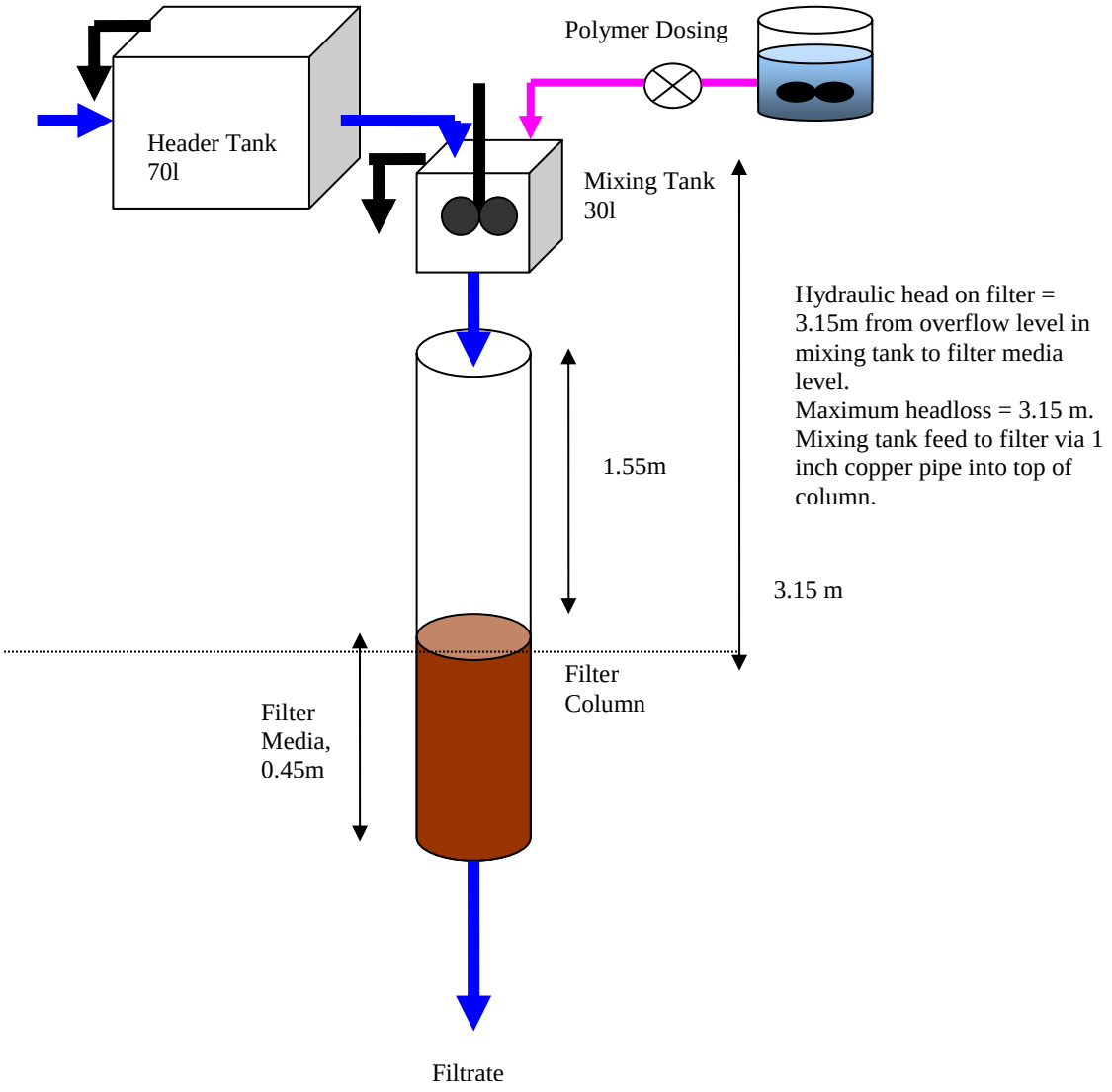


Figure 16 Diagram of pilot filter column with polymer dosing unit

The inlet mono-pump was chosen in order to provide the filter rig with sufficient flow and because it was thought that a mono-pump would subject the floc to less shear forces than a centrifugal pump. The pump was left running continuously with the header tank set to overflow constantly. The mixing tank was fed by gravity from the header tank, and contained a paddle type stirrer operating at 400 rpm. The polymer solution was dosed into the mixing tank. It was assumed that the mixing tank provided adequate mixing for the polymer dosing as the filter run data showed good consistency as did the PDA readings generated from samples taken from the mixing tank. The mixing was tested by measuring the pH and zeta potential at different locations within the mixing tank during addition of alkali into the mixing tank (using a constant dose of alkali). The results from this test indicated that the mixing of the alkali was very good and therefore the unit would be suitable for dosing of a dilute polymer solution. The polymer stock solution was kept dilute to aid the mixing of the polymer solution with the plant water. The mixing tank was also setup to overflow in order to provide a constant flow through the mixing tank, as the flow through the column declined; this was essential in order to keep the polymer dosing accurate. The residence times of the key tanks in the pilot plant are shown below in table 10

Vessel	**Purpose**	**Volume (l)**	**Approximate residence Time (min)**	**Mixing type**	**Overflow**
Polymer stock tank	Keep polymer solution well mixed	6	500-600	Magnetic stirring	no
Header tank	Provide a constant head tank	70	2-3	none	constant
Mixing tank	Provide adequate mixing of polymer with plant water	30	10	High-speed stirrer (400rpm)	constant
Column (above media)	Convey water to filter media	33	10	none	no

Table 10 Summary of pilot plant tank sizes and residence time

Part 3.9 Pilot Filter Backwash Parameters

The pilot filter was designed to be as comparable as possible to the main plant filters, there was an obvious in-compatability with the pilot filter unable to flow modulate, but declining flow mode was thought to give useful results. The backwash procedure is known to have an impact on the filtration performance by contributing to filter ripening turbidity spike on start-up (Cranston and Amirtharajah, 1987). The effect of a poor backwash procedure is generally thought to contribute to a larger return to service turbidity spike due to backwash remnants (Amirtharajah and Wetstein, 1980) and is therefore to be avoided. The main plant filter backwash design was based on achieving 15-20% bed expansion, which is a common design parameter according to best practice as identified in Cleasby and Logsdon, (1999). The main plant filters were also capable of temperature compensated backwash flowrates to ensure the same degree of expansion as the viscosity of water changes with temperature. The pilot filter backwash parameters were scaled down from the main plant, but the regime was not changed according to temperature, as media loss was not an issue on the pilot rig. The backwash regime used on the pilot filter plant was calculated as follows based on 15ºC:

Pilot column media surface area: $\pi d^2/4 = \pi * 0.138^2/4 = 0.015\ m^2$

Air Scour Flowrate

Air scour flowrate (Albert WTW main plant) = $50 m^3/m^2/hr$

Pilot plant air scour Flowrate = $0.015*50 = 0.75\ m^3/hr = 12.5$ l/min

Low Rate Upwash

Low rate upwash (Albert WTW main plant) = $7.65 m^3/m^2/hr$

Pilot plant upwash rate = $7.65*0.015 = 0.115\ m^3/hr = 2$ l/min

High Rate Upwash

High rate upwash (Albert WTW main plant) = $24.9 m^3/m^2/hr$

Pilot plant high rate upwash = $24.9*0.015 = 0.4\ m^3/hr = 6$ l/min

The backwash regime on the pilot filter plant mirrored that of the main plant and was as follows:

1. 4 mins air scour
2. 4 mins air and low rate water upwash (collapse-pulsing)
3. 8 mins high rate upwash
4. Rest period of 5 mins

Part 3.10 Design of polymer dosing unit

The polymeric flocculants were manufactured by SNF Floerger, and all came in solid form. The stock solution was made up to a concentration of 8 g/l in accordance to the manufacturer's guidelines, which indicated that this concentration would be stable for a month if kept in a cool dark place. All stock solutions were made up following the same procedure and disposed of after a month as per the procedure detailed in appendix 3. The polymer dosing system is shown in figure 17.

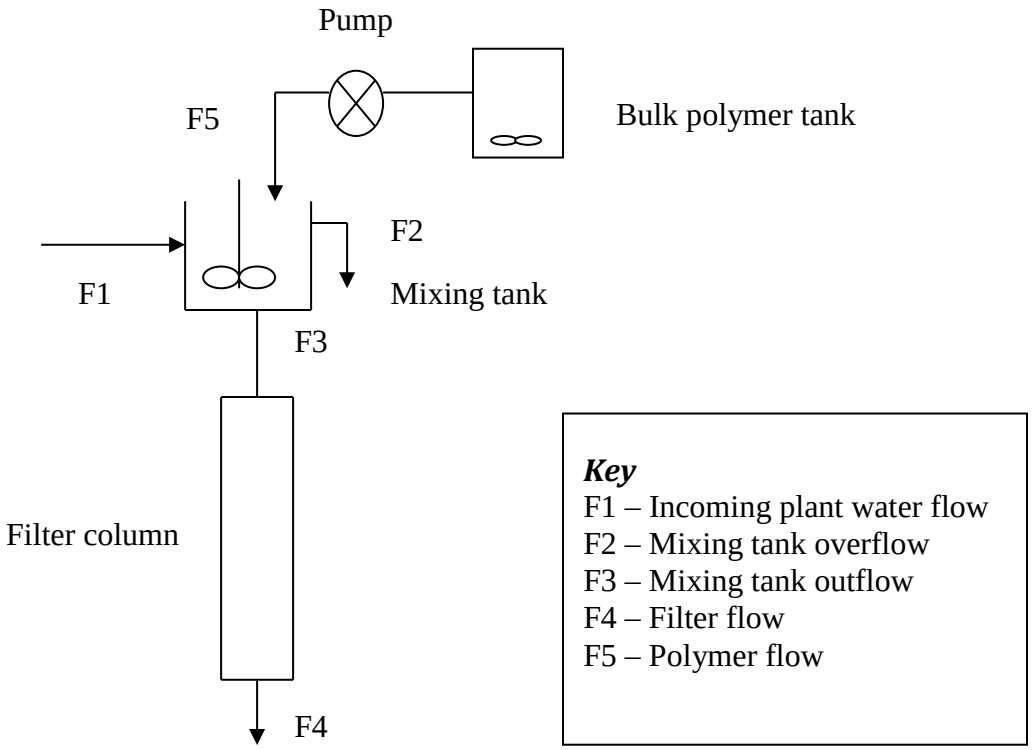


Figure 17 Pilot filter plant process flow diagram

A mass balance was carried out over the mixing tank to determine the required bulk solution concentration and the pump speed. The mass balance equation below shows that either one of flowrate or bulk solution concentration has to be decided before the equation can be solved. In this situation it was decided to keep the pump rate constant at a reasonable rate that would ensure

the 6 litre polymer bulk solution tank didn't empty overnight. It was decided that the polymer bulk solution should last 10 hours, which equates to a pump speed of 0.01 l/min.

Mass balance around mixing tank at start of run:

Input = Output + Accumulation

$F1 + F5 = F2 + F3$

$F3 = F4$ (Filter column inflow = filter column outflow) = 1.5 l/min

$F2 = 1.5$ l/min (flow measured manually from overflow pipe using measuring cylinder)

$F3 + F2 = F1 = 3$ l/min

Mass balance with respect to polymer at start of run (X denotes concentration of polymer in flow stream in mg/l):

$F1X1 + F5X5 = F2X2 + F3X3$

$X1 = 0$ mg/l (no polymer in plant treated water)

$F5X5 = F2X2 + F3X3$

$X2 = X3$

$F5X5 = 3*X3$

$X5 = 3X3/F5$

For a desired dose of 0.02 mg/l and a pump rate of 0.01 l/min, the bulk solution concentration would need to be: $(3*0.02)/0.01 = 6$ mg/l

At this rate the bulk tank lasted for 10 hours, which was sufficient for the duration of an overnight run. The mixing tank overflow was wasteful but essential to provide a constant polymer dose as the filter was set up to operate in declining flow mode, which meant that the flowrate through the filter declined as the filter clogged with removed particulate. In this case, the flow out of the mixing tank declined as less was allowed through the column, and therefore the mixing tank overflow rate increased proportionally considering that the same hydraulic head was available to the mixing tank throughout the runs. The total flow passing through the mixing tank remained the same throughout the run and the polymer dose applied was constant. The polymer dose was changed by varying the concentration in the bulk tank which involved diluting the stock solution down to the calculated concentration. Dilution into the bulk tank was carried out directly using micro-pipettes and volumetric flasks to ensure a high degree of accuracy of polymer dose. Analytical grade weighing scales were also used to weigh out the polymer powder used to make the stock solution.

Part 3.11 Calibration and maintenance of monitoring equipment

The electrical equipment on the filter rig was all calibrated and checked for electrical safety prior to use and periodically during the period of operation. The monitoring equipment provided the basis for assessing filter performance, and the accuracy and frequency of data recording was therefore considered to be of great importance to the project. The filter run lengths were anticipated to last >12 hours and therefore the monitoring equipment setup was designed to operate and record data continuously. The filter rig could therefore be left overnight to continue recording data from filter runs. Signals were taken from the monitoring equipment and wired into a data logging circuit which converted the 4-20 mA signal into a digital signal which was then displayed on a laptop as a real-time numerical output. The equipment signal was calibrated at the start of the project in order to be able to calculate the equipment's actual output from the voltage output recorded on the laptop. The Pico-log software was only able to take inputs between 0-2V, and so a suitable 100 Ohm resistor was placed into the circuit to enable the circuit to process the 4-20 mA signals. The particle counter came with its own data logging interface and WQS Vista software. The data from each run was downloaded after each run, and transferred to Excel spreadsheet form whereupon graphical analysis of the trends was possible. The particle sensor was purchased as new at the start of the project and it was therefore calibrated by the manufacturers who recommended that the sensor should be calibrated every 2 years. The project duration was within 2 years and therefore the sensor wasn't calibrated during the research. The GLI turbidimeters were cleaned and calibrated monthly using the GLI calibration cube. The Rosemount pH probe was also cleaned and calibrated monthly using the directions as detailed by Rosemount. The probe was calibrated via a 2 point buffer technique, using pH 4 and pH 7 buffer solutions. The Endress and Hauser differential pressure transmitter was bled when required and did not require calibration or cleaning. The Mag-Flow flowmeter was calibrated at the start of the project and manual checks were made frequently to check that the output was accurate. Manual checks involved measuring the flow volume output over a timed period. All electrical equipment was safety tested prior to the project according to Yorkshire Water policy. The filter column and respective tanks were cleaned when necessary. The pilot plant instrumentation and positioning is shown in figure 18.

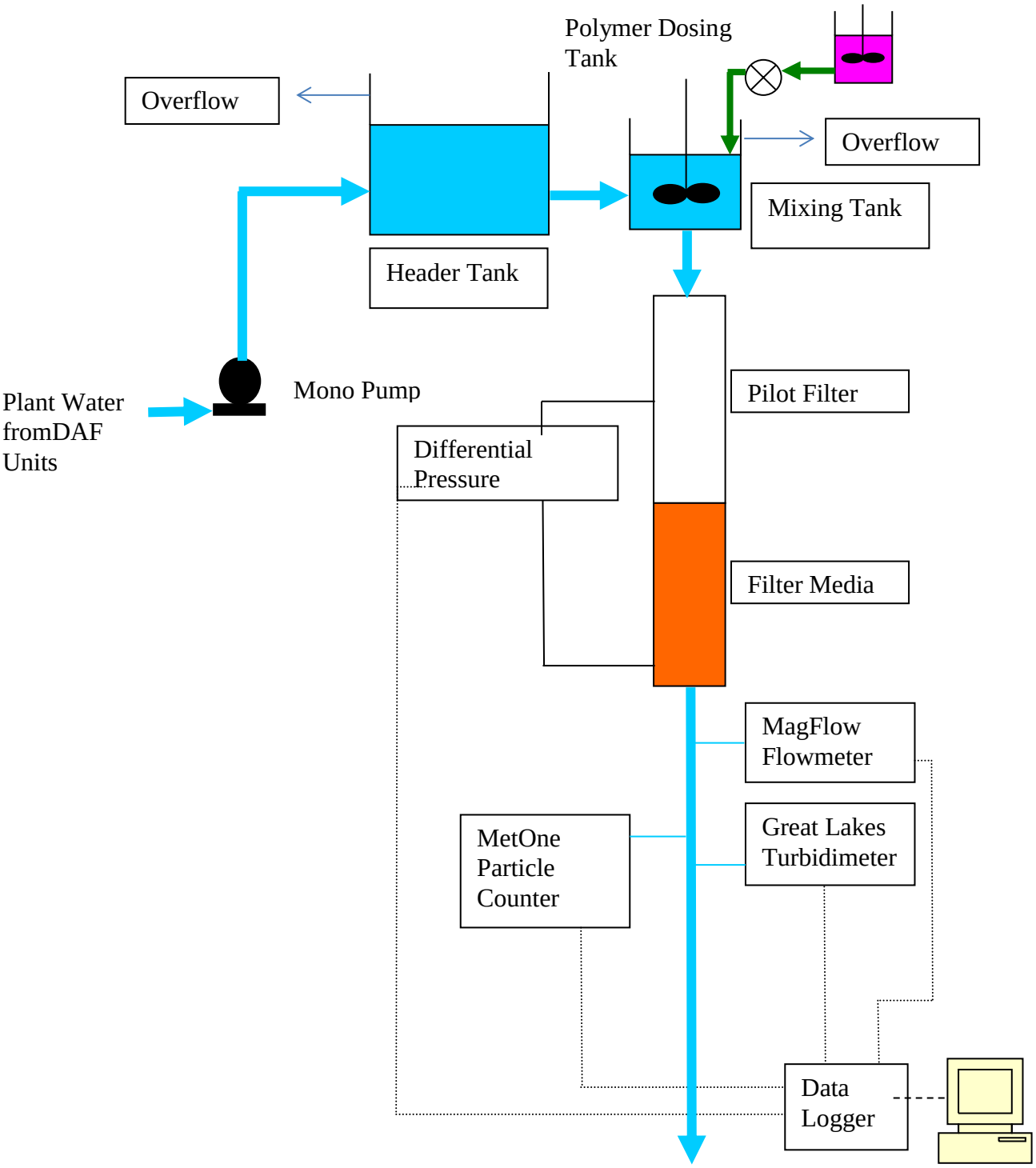


Figure 18 Pilot Filter Rig Schematic showing instrumentation

Part 3.12 Analysis of Filtration Particle Count and Turbidity Trends

Pilot filter experiments comprised a major part of this research work, as one of the aims of the project was to relate floc physico-chemical properties to filter performance; with a focus on causes of breakthrough at low headloss. At the start of the filtration experiments, the design of the pilot filter was set to model Albert WTW filters with the exception of constant flowrate which could not be achieved. Initial work carried out in the summer months with a full bed depth filter didn't show any filter breakthrough as seen in figure 19. This is an example of a filter run carried out on the pilot filter using the full 0.9 m bed depth using water taken directly from Albert WTW DAF outlet prior to lime dosing. The decision was made to reduce the filter media depth by a factor of 2 in order to encourage earlier breakthrough.

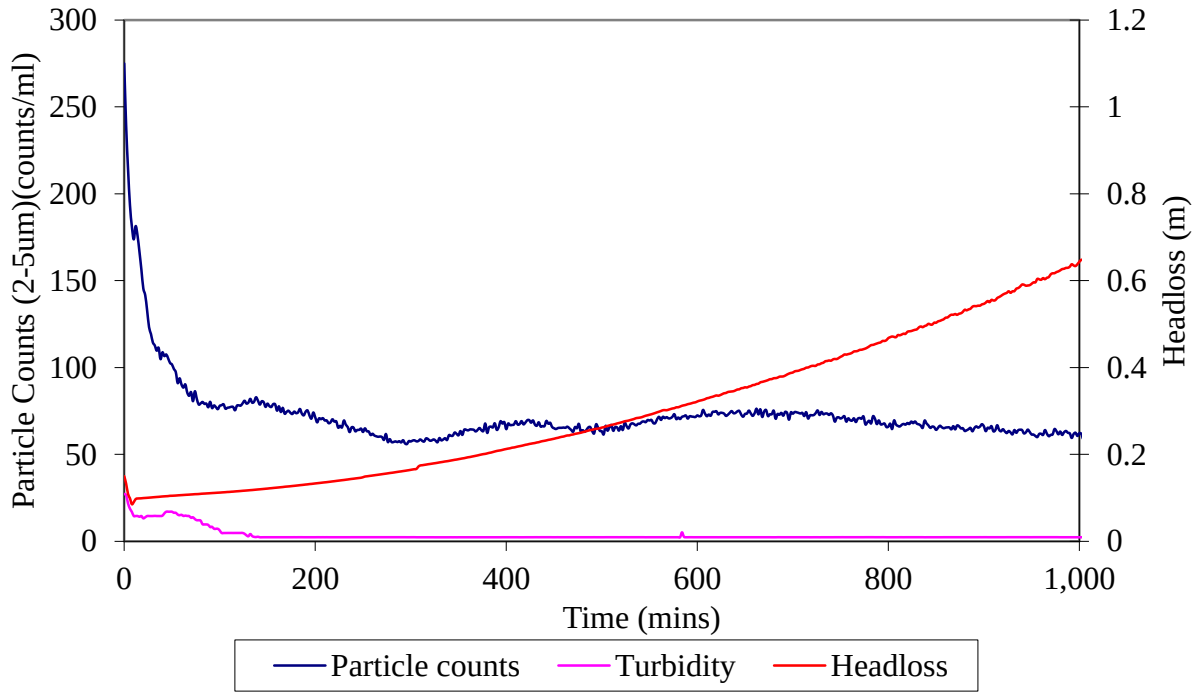


Figure 19 Filter performance using full 0.9m bed depth

Figure 20 shows that this was successful as breakthrough was observed during the reduced bed depth filter run, and thereafter all of the filtration experiments were operated at a reduced bed depth compared to the main plant filters. The filtration curve in figure 20 shows a classic

"bathtub" shape, the main features of which have been explained by Amirtharajah and Wetstein (1980) and are discussed and illustrated in Chapter 2. The filter was set up to operate in declining flow, and therefore the most sensible x –axis parameter to compare filter runs was the filtered volume. This enabled comparison between filter runs, as the rate of flow decline couldn't be guaranteed as constant although significance testing as performed on this parameter when comparing runs. The filtration experiments using the DA20 had to be carried out during conventional working hours, and as the DA20 pilot plant took at least 1 hour to start-up to steady state, the filter runs were limited to approximately 5 hours duration. The filter baseline comparator was determined as the stage when the filtered turbidity reached a flat-line after ripening, this was generally reached by 250 litres for most experiments and therefore the water quality at this point in the filter runs was compared. From a calculation of the residence time of the pilot filter (shown in table 4), it was calculated that the filter would be "ripening" with influent water after the first 10 minutes. This enabled the overall picture to be assessed after initial assessment of filter run performance from studying the real-time trends.

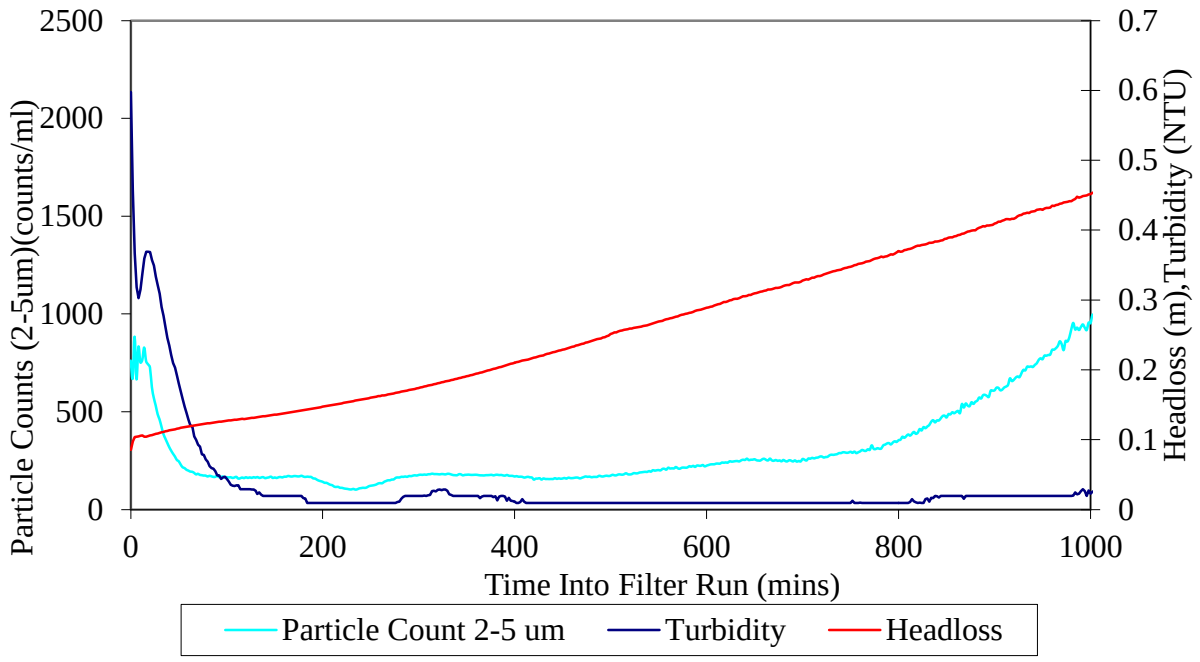


Figure 20 Filter performance using 0.45 m reduced bed depth

Part 3.13 Statistical analysis techniques

The T-test is a commonly applied statistical technique for comparing 2 sample populations based on the assumption that a comparison of the mean from sample 1, and the mean from sample 2 would show that overall the two sample sets originated from the same distribution. This test is in essence compares the actual differences between 2 samples means in relation to the variability within the sample set. In this work, one of the main uses of this comparative measure was to assess the water quality between experiments when investigating the same effect such as a change in coagulant dose. In a real natural water system, this was considered important when establishing trends with uncontrolled variables within the experiment. This was carried out in order to take into account the following:

- Raw water quality variability
- System and parameter sensitivity to controlled changes (change in coagulant dose for example)
- Operator error

The following is a worked example of a comparison between coagulation pH 3.5 and pH 4.5 using 10 mg/l Ferripol XL as Fe^{3+} with respect to residual UV_{254} absorbance. The objective of the T-test worked example was to identify if the residual UV_{254} absorbance was significantly different between the two runs. The T-test calculations were carried out using Microsoft Excel. The 2 sets of data being compared were assumed to be related as they were measures of the same parameter. This made the T-test a "paired" T-test. The other specification was that the test was 2-tailed, and that there was no bias in the distribution of the data. Considering the large quantity of data to be processed, Excel was used throughout to calculate the t-value, and more importantly the probability (p-value) of the calculated t-value arising from chance. This value was used to classify whether the data was significantly different. If $p < 0.05$ then the chance was considered remote (1 in 20) and therefore significantly different. If $p > 0.05$, then the chance was considered less remote and therefore not significantly different. The results in table 12 are an example of the Excel T-test calculation function for the above data in table 11.

The P value shown in table 12 represents the probability that the calculated t-value would have been obtained by chance, which is extremely remote and therefore should be considered to be significantly different.

Sample Number	Residual UV_{254} absorbance at pH 3.5 and 10 mg/l Ferripol XL as Fe^{3+}	Residual UV_{254} absorbance at pH 4.5 and 10 mg/l Ferripol XL as Fe^{3+}
1	14	6
2	14	4
3	15	4
4	14	4
5	13	4
6	14	4
7	14	4
8	14	4
Mean (X)	**13.9**	**4.08**
Variance (σ^2)	0.28	0.52
Population (n)	8	8
Variance of difference between the 2 means (σ_d)	=(0.28/8) = 0.035	=0.52/8 = 0.065
Sum of variance of differences	=0.035+0.065 = 0.1	
Square Root of above	=SQRT (0.1) = 0.32	
Calculated t- value	=(13.9-4.08)/0.32 = **31**	
t –value at 7 degrees of freedom and probability 0.05 (found from t-Test lookup tables)	= **2.37**	
Is calculated t-value > t-value at 7 degrees of freedom and probability 0.05?	31 >> 2.37 therefore significantly different	

Table 11 T-Test value calculation example

t-Test: Paired Two Sample for Means		
	Variable 1	*Variable 2*
Mean	13.9	4.0
Variance of difference	0.33	0.59
Sample Population	8	8
Degrees of freedom	7	
t - value	29.6	
P(T<=t) two-tail	1.2E-08	
t Critical two-tail	2.36	

Table 12 Example of Excel T-test calculation outputs

Where inter-relationships were studied to identify causal trends such as in the experimental work in Chapter 6; the regression analysis tool in Excel$_{TM}$ was used to compute the regression coefficient and the F-test probabilities.

Part 3.14 Discussion of Experimental Method

It was obvious from the conception of the project that there would be parameters that would not be able to be controlled as rigorously as model systems in a laboratory involving systems of known quantity of synthetic humic acid/kaolin suspension. The system involving natural raw water is the most complex to control and therefore interpret. The implications of this are discussed here. The most obvious control parameter is the quality and nature of the organic material present in the raw water. The project was mostly carried out on-site at a treatment works over two years, and during this period the water quality was not consistent. The quantity of organic matter present also varied over the project duration, in some cases the quality varied from day to day during periods of heavy rainfall. Jar tests were carried out on the same bulk volume of water for each parameter investigated in order to compare results with the same water quality. Various jar tests were carried out over the project duration and it wasn't practical to carry out all the tests on the same bulk volume of water, which made some comparisons between the jar tests difficult. The jar tests were designed to give useful information about the coagulation performance and floc strength of the systems concerned so the need for comparisons between jar tests was reduced. The jar tests were also designed to test the effectiveness of the PDA, as its' use with natural raw waters had not been established at the time of the project design. It was important to achieve repeatability of the jar tests under the same conditions to establish that the experimental method was suitable and the PDA worked well with natural waters. One of the project's aims was to evaluate the effect of floc reformation and strength factors on filter performance on a real water system.

The concept that floc strength plays a part in filter performance is not novel, but is very difficult to evaluate without a proven method of measuring floc strength. There are also many ways of defining floc strength. The breakage jar test using the PDA optical flocculation monitor is a proven technique for evaluating floc strength and reformation capability with kaolin-based systems and other synthetic waters. Gregory and Yukselen (2002) used it successfully to show that some polymeric additives give rise to reversibly formed floc. The PDA output (floc index) is representative of the floc size and therefore by comparison of the floc size before and after breakage, a measure of the floc strength can be obtained. The data-logging interface allowed the PDA output to be represented numerically as well as graphically thereby creating the opportunity to generate numerical representation of:

- floc strength factor
- floc reformation factor.
- flocculation rate
- maximum floc size

Analysis of the flocculation curves using the data-fitting software TableCurve enables the ratio of the floc index after breakage to floc index before breakage to be computed. This ratio can be used to compare jar test results. The procedure for evaluating floc strength was therefore established as described above and experimental work then focused on finding methods for improving floc strength and filter performance. This work was carried out using the pilot filter rig shown in figure 21 in combination with the breakage jar tests. The water entering the pilot filter rig was taken from the main plant and contained NOM/ferric floc at a pH of 4.2-4.5. This floc has been subjected to high shear stresses throughout the process and was therefore very fragmented by the time it reached the plant filters and it was thought that this contributed to filter breakthrough at low headloss, and therefore a method of strengthening the floc was sought. The strength of the floc could be improved by optimising the coagulant choice at the primary coagulation stage or by utilising flocculants. The experimental setup was only suitable for flocculant dosing prior to filtration as the DA20 pilot plant was not available for the length of time required to investigate different coagulant options, and it wasn't practical to try different coagulants on the main plant on an experimental basis.

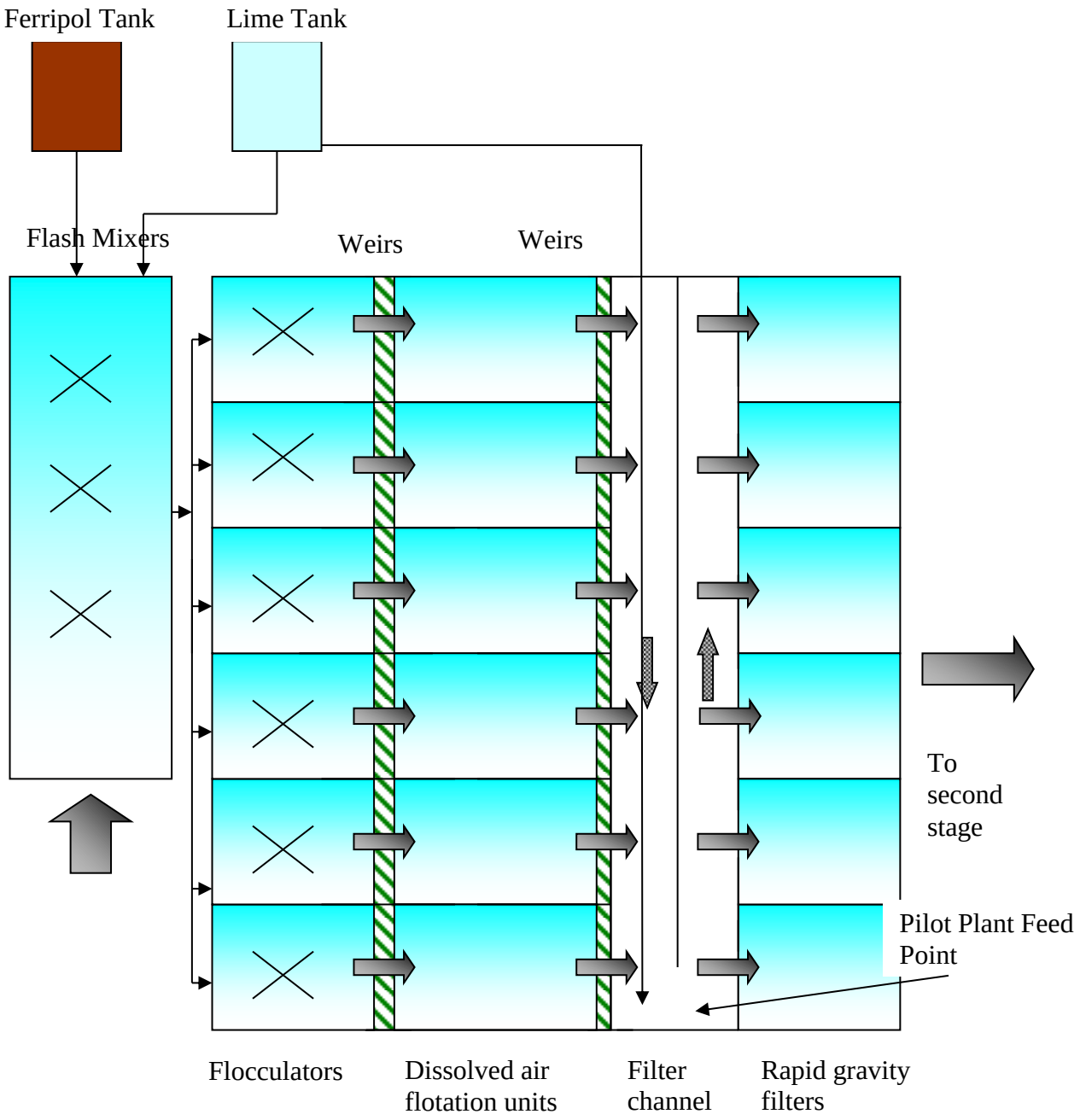


Figure 21 Plan of Albert water treatment plant primary stage showing pilot plant feed point

Chapter 4 The effect of coagulant type on floc properties

Part 4.0 –Jar tests carried out at UCL laboratories using the PDA and different coagulants March –April 2002

The experimental work presented in this chapter was carried out at UCL laboratories using bulk samples of raw water sent from Yorkshire Water's Albert WTW raw water reservoir. The purpose of the experiments was to establish that the PDA could be used to monitor a natural raw water as previous studies had focussed mostly on synthetic water systems (Yukselen and Gregory, 2002). The experiments were designed to study the properties of floc formed with different types of coagulant, and to do this the effect of coagulant dose on NOM removal was evaluated as well as floc size, strength factor and reformation factor at the optimum coagulant dose (optimum dose was determined by best NOM removal).

Part 4.0.0 Raw water batch quality

Raw water was sent in three batches of 15 litres to UCL laboratories directly from Albert WTW impounding reservoir and the UV_{254} absorbance, pH, and turbidity of the batches was recorded over 7 days. Figure 22 to 24 shows the variability in UV_{254} absorbance, pH and turbidity respectively for batch 1 over a 7 day period of storage under refrigerated conditions at 5°C. Three samples were measured daily from which the standard error was calculated.

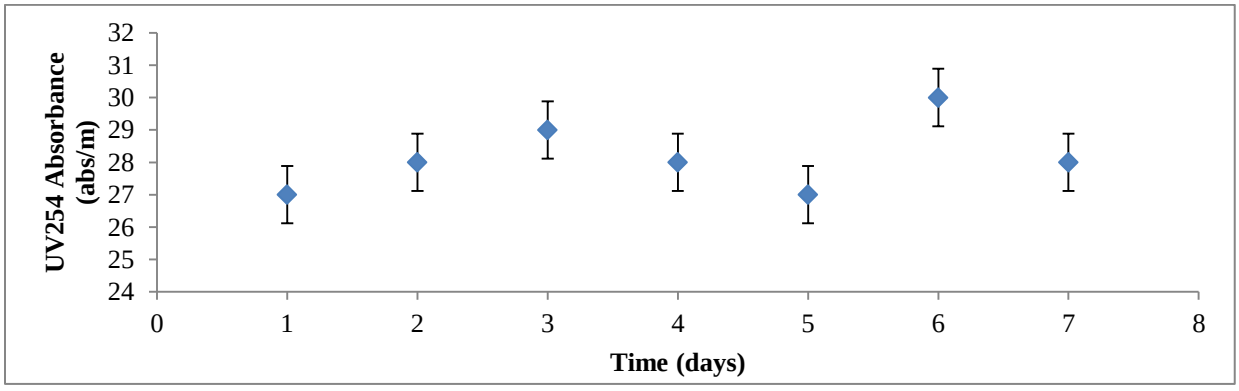


Figure 22 UV_{254} absorbance over 7 days under refrigerated conditions (raw water batch 1)

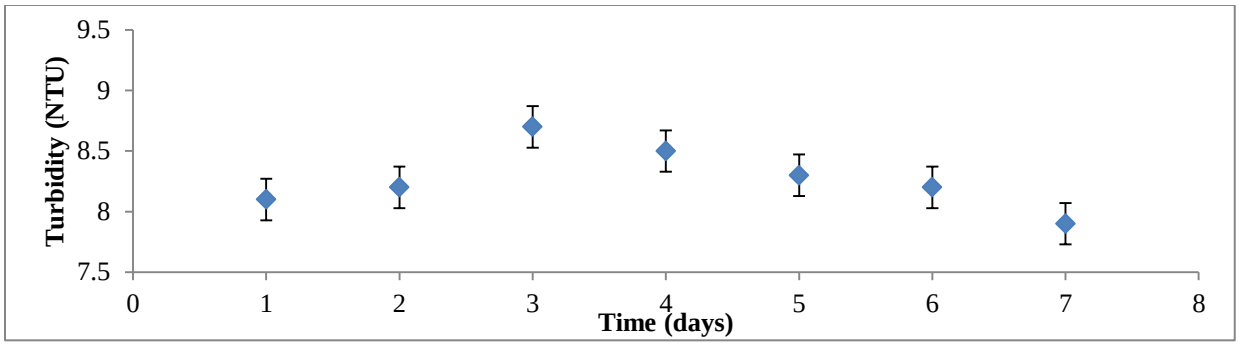


Figure 23 Turbidity over 7 days under refrigerated conditions (raw water batch 1)

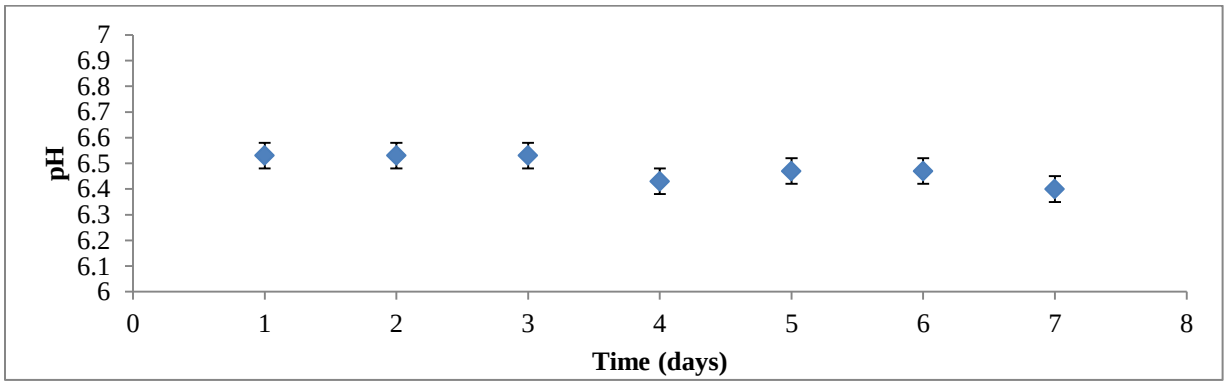


Figure 24 pH over 7 days under refrigerated conditions (raw water batch 1)

The measured water quality parameters showed a reasonable consistency over the 7 day period indicating that the storage of bulk samples didn't impact greatly on the water quality parameters, and that the water quality was reasonably stable over the experimentation period. The three batches from Albert WTW reservoir varied with respect to UV_{254} absorbance and pH but little variability was observed in the turbidity measurements as shown in figure 25.

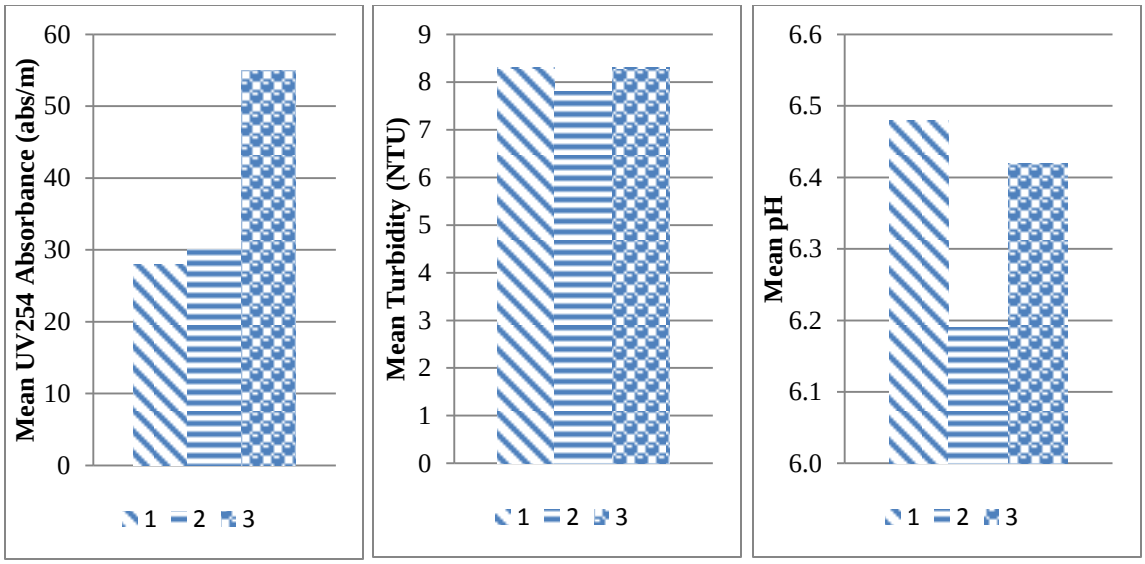


Figure 25 Mean raw water quality of the three 15 l batches

Figure 24 shows that the first two batches of water from Albert WTW were very similar with respect to UV_{254} absorbance measurements but the third batch had a much higher level of colloidal material, which was reflected by a UV_{254} absorbance reading approximately 40% higher than the previous two batches but with little difference in the turbidity measurements. The DOC was also recorded as 7.9 mg/l for both batch 1 and batch 2, but not measured on batch 3 due to loss of sample. The SUVA of the raw water in batches 1 and 2 was 3.5 and 3.7 $m^{-1}L/mg$ C and therefore could be considered similar in terms of the nature of the NOM being dominated by the hydrophobic fraction (Edzwald and Tobiason, 1999). This variation in the raw water organic material between batches 1 and 2, and 3 was to be expected from operational experience. This highlights the need to establish a method to identify a suitable relationship between raw water quality parameters, coagulation conditions and plant performance. A period of increased rainfall was identified as the reason for the increase in the raw water UV_{254} absorbance in batch 3, other reasons for sudden changes in raw water quality can also be attributed to changes in raw water source from the onsite impounding reservoir to direct abstraction from the catchment. The changes in raw water quality can happen very quickly and if the treatment process doesn't respond effectively it is certain that there would be deterioration in the final water quality.

It is therefore crucial that the treatment process is robust enough to cope with these fluctuations in raw water quality, without affecting the final water quality to the customer. It is for this reason that this research project's first experiment, was to evaluate the coagulation performance with different coagulants by using jar tests and breakage jar tests and evaluating the humic substance removal and floc characteristics. The primary objective of this set of experiments was to determine suitable coagulants and doses for good removal of UV_{254} absorbing compounds; and to assess the potential benefits of using polymeric additives which have previously been found to improve floc properties with kaolin based systems (Gregory and Yukselen, 2002). In their work they found that Zetag 64 and polyDADMAC produced floc with an improved reversibility compared to alum.

Part 4.1 – Coagulation and flocculation using single coagulants systems at 22ºC

Part 4.1.0 Coagulation and flocculation at pH 4.5 using ferric sulphate

Ferric sulphate was sourced from Sigma Aldrich, and was of analytical grade purity. The solutions were made up to a 1g/l concentration on a daily basis as hydrolysis of the solution occurred if left over time. The temperature in the laboratory was reasonably constant at 22ºC at the time of experimentation and the water was left to acclimatise to room temperature before staring the jar tests. Four doses of ferric sulphate were used and each dose was repeated three times for reproducibility purposes. The optimum dose was identified by measuring UV_{254} absorbance removal with each ferric dose, and flocculation performance was evaluated via analysis of the flocculation curves obtained from the PDA. Analysis of the results indicated a suitable dose to perform the breakage jar tests with as per the methodology discussed in Chapter 3. Figure 26 shows the UV_{254} absorbance removal trend with increasing dose. The water used for this experiment came from the same batch and therefore the residual UV_{254} absorbance is plotted rather than the removal percentage.

Figure 26 shows residual UV_{254} absorbance decreased with incremental coagulant dose up until the point of over-dosing, which is seen on this graph at 14.1 mg/l. At this point the residual UV_{254} absorbance deteriorated as the overdose led to re-stabilisation of some of the colloidal material. Figure 26 indicates that a dose of 10.6 mg/l was a suitable dose for achieving good removal of colloidal organic material as measured by UV_{254} absorbance at pH 4.5 and 22ºC for this sample of raw water and the dose range applied. Removal of UV_{254} absorbance using 10.6 mg/l as Fe 3+ yielded a good result of 0.4 abs/m which was well within the industry standard of <5 abs/m. This indicated that the colloidal material was mainly hydrophobic in order to achieve such good removal with ferric sulphate. This concurs with the SUVA results from batches 1 and 2 which were within the range thought to be dominated by the hydrophobic fraction.

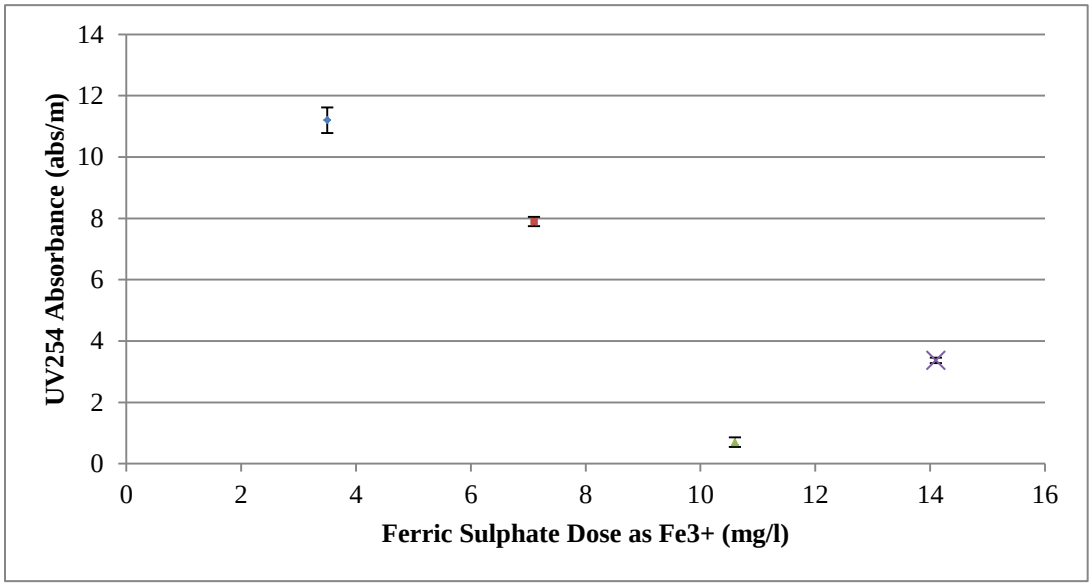


Figure 26 Residual UV_{254} absorbance and ferric sulphate dose at coagulation pH 4.5, 22ºC (raw water batch 1 – 28 abs/m)

Research carried out by Sharp *et al.* (2006) on the same raw water source during October 2003 showed that the raw water from this source comprised of an average of 66-75% HAF and FAF fractions. This was consistent throughout the year. Their results also showed that heavy rainfall events led to an increase in both hydrophobic and hydrophilic components, which resulted in a change in the polarity balance of the raw water. This could explain some of the treatment problems experienced at Albert WTW, as it is known that the hydrophilic fraction of humic acid isn't well removed by conventional hydrolysing coagulants.

The low standard error of the raw water measurements indicated that the experimental method was fairly consistent, and that the trends observed were not due to experimental error. It is to be expected that the accuracy of the coagulant dosing and the measurement of the volume of raw water would give rise to some degree of experimental error, but the actual error observed suggests that this was not excessive and the results can therefore be interpreted with a reasonable degree of reliability although the author acknowledges that a greater number of repeats would have been statistically superior. The dosing of coagulant and alkali/acid was carried out using volumetric pipettes which is one of the most accurate methods of dispensing chemical solutions. Pipettes were calibrated before the experimental work as mentioned in Chapter 3. Figure 27 shows the quantity of alkali required to achieve a coagulation pH of 4.5 at the given doses of Ferric as Fe^{3+}.

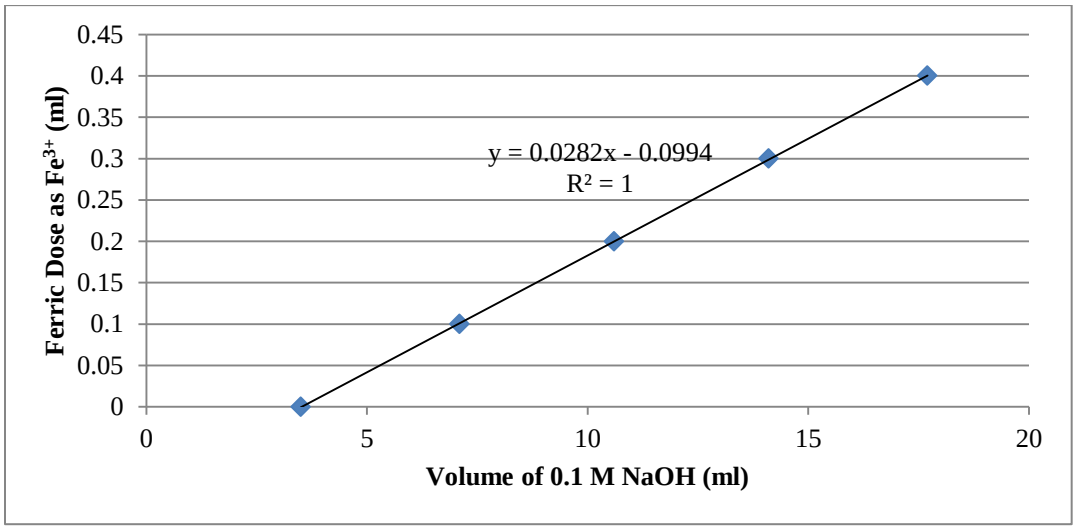


Figure 27 Relationship between applied Ferric dose as Fe^{3+} and quantity of NaOH to maintain coagulation pH 4.5

As would be expected, the relationship between the Ferric dose and alkali was linear. The results from the dynamic flocculation monitoring are discussed next.

Figure 28 illustrates the graphical form of the dynamic flocculation data generated from the PDA. The curves follow the shape of the Sigmoid function, with an exponential phase occurring shortly after the onset of flocculation is detected. All curves exhibited a lag phase, or delay in the onset of flocculation which is due to the process of charge destabilisation of the organic material prior to flocculation. The gradient of the flocculation index curve increased as the dose approached the optimum of 10.6 mg/l as Fe^{3+}, but then decreased as the dose was increased to 14.1 mg/l as Fe^{3+}. The flocculation rate is thought to be indicative of good coagulation performance and therefore the fastest growing flocs should correspond to the best UV_{254} absorbance removal. This was seen to be the case in this single primary coagulant trial using ferric sulphate. The reasoning for the link between flocculation rate and UV_{254} absorbance removal is that at the optimum dose (or conditions), the charge on the organic material can be destabilised quickly and the resulting floc precipitates fast as the resistance due to repulsive effects is minimised. It is therefore to be expected that the flocculation rate should be fastest at the most suitable ferric dose

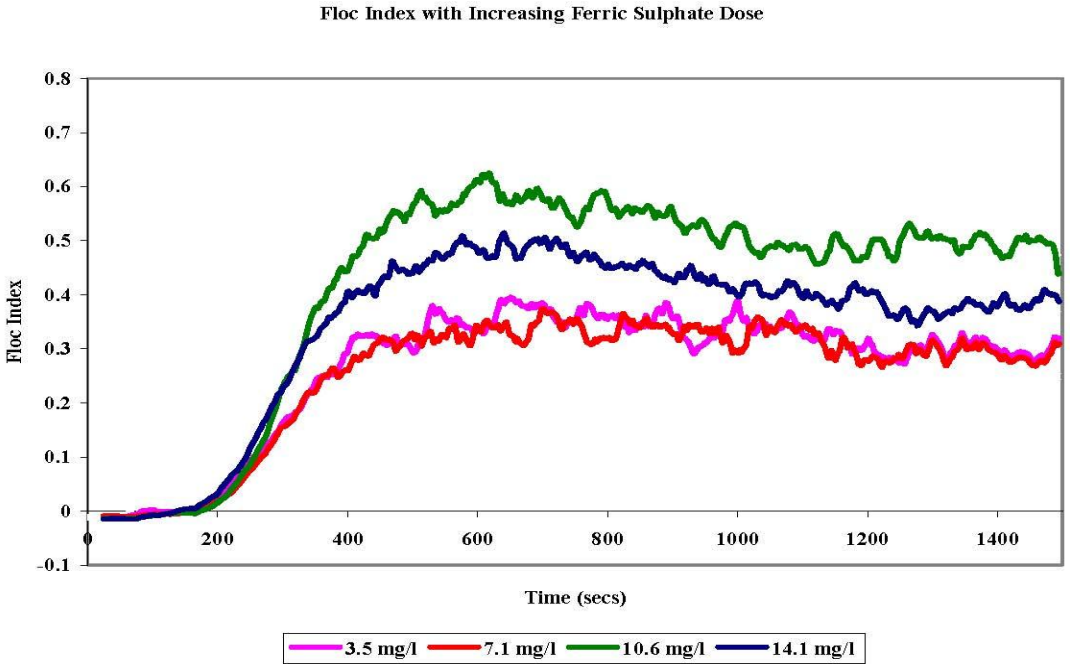


Figure 28 Dynamic flocculation curves using a range of ferric sulphate doses *

***Dose is expressed as mg/l as Fe^{3+}**

Figure 29 shows the general trends between ferric dose, mean UV_{254} absorbance removal and mean dynamic flocculation parameters, R_{FI} and FI_{max}.

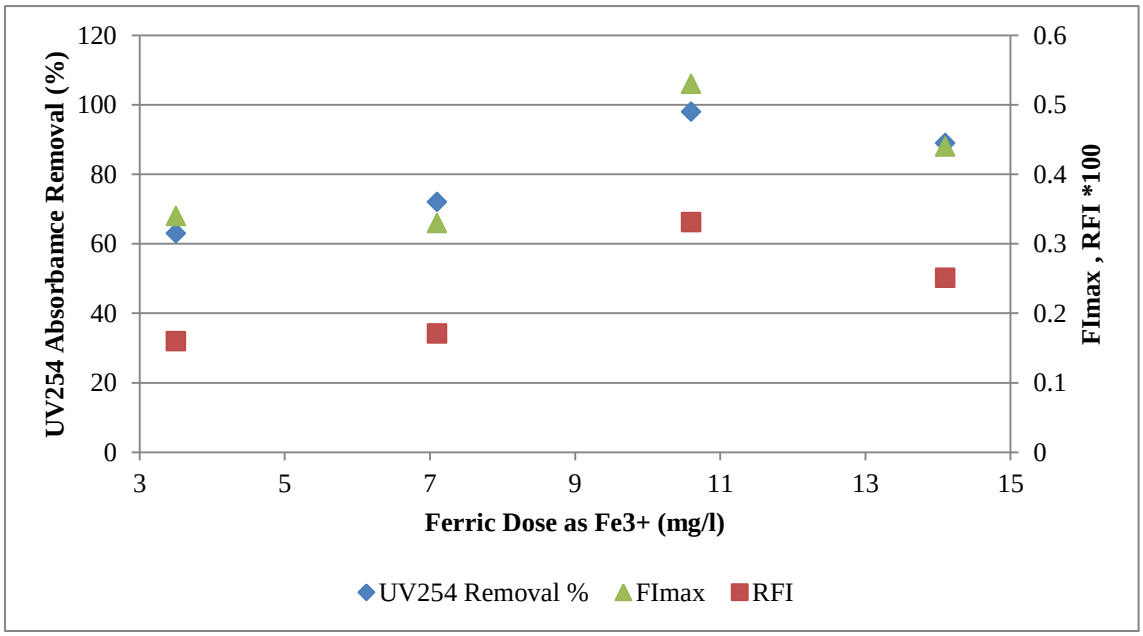


Figure 29 Dynamic flocculation parameters FI_{max} and R_{FI} and ferric dose and UV_{254} absorbance removal, pH 4.5, 22°C (Raw water batch 1 – 25 abs/m)

Part 4.1.1 Coagulation and flocculation using polyDADMAC at 22ºC and pH 6.2

The jar test procedure as described in Chapter 3 for organic primary coagulants was followed. The main difference in procedure from those followed with the ferric sulphate tests was that the pH was not changed with NaOH from that of the raw water and a longer rapid mix period of 30 seconds was incorporated to ensure adequate adsorption of the polymeric additive onto the humic acid. This was based on work by Gregory and Yukselen (2002) who found that the time taken for hydrolysis and adsorption of polymeric additives such as polyDADMAC onto synthetic humic acid was much greater than for hydrolysing metal coagulants. There are many different types of polyDADMAC solutions commercially available and for these experiments an Allied Colloid's solution called MagnaflocTM was used as it has a high charge density and previous work by Gregory and Kam (1999) has evaluated the performance of the cationic additive as measure by streaming current detection. The raw water used in these tests was taken from batch 2 which had a similar raw UV_{254} and SUVA measurement to batch 1.

Figure 30 shows the residual UV_{254} absorbance trend versus the polyDADMAC dose. This shows that the trend tended towards a decrease in residual UV_{254} absorbance as the dose of polyDADMAC increased, with very little benefit achieved by increasing the dose to over 5 mg/l. Poor flocculation was observed at doses above 5 mg/l suggesting that these were over-doses. The optimum dose according to UV_{254} absorbance measurements was seen to be around 5 mg/l as this dose gave rise to the best removal percentage of 77% and visible flocculation. The residual seen at 5.8 mg/l was erroneously low as it was noted in the jar test that there were no flocs formed as shown in figure 30. This result could be explained by the formation of a cationic complex which adhered to the 0.45µm membranes used to prepare the samples and therefore gave a false residual.

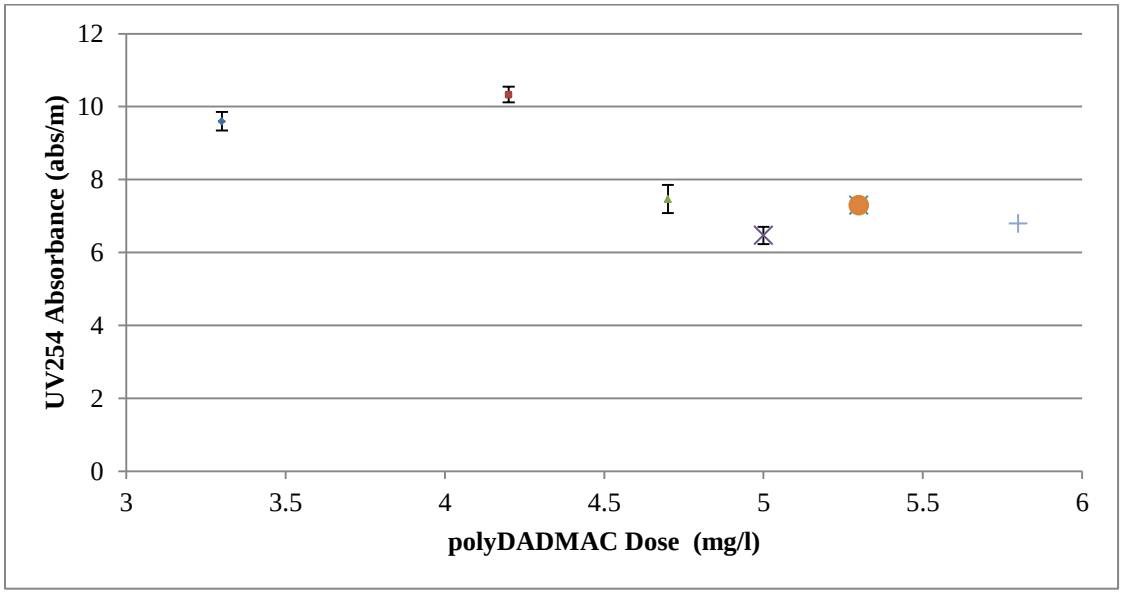


Figure 30 Residual UV_{254} absorbance using polyDADMAC, pH 6.2, 22ºC (Raw water batch 2 – 30 abs/m)

Figure 31 illustrates the dynamic flocculation process with each dose of polyDADMAC. The curves show that there was some flocculation at the lowest dose of 3.3 mg/l, as there was a small increase in flocculation index throughout the test but no flocculation occurred at the highest dose of 5.8 mg/l.

The time taken to reach the plateau (FI_{max}) value of the flocculation index tended to increase as the dose increased between 4.2 – 5.3 mg/l, but the magnitude of the FI increased. The de-stabilisation time of the colloidal material (quantified by the time taken for detectable flocculation to occur) was much longer than that with hydrolysing metal salts such as ferric sulphate, which has been reported previously by Gregory and Yukselen (2004). Comparison of the flocculation rate R_{FI} between the ferric based coagulant systems and those dosed with polyDADMAC showed that the ferric systems flocculated 100 times faster than with polyDADMAC. It has been hypothesised that the reason for this increased time period is due to the slower adsorption of the organic polymer molecules onto the humic acid. In reality a rapid onset of flocculation is desirable, as this reduces the volume and energy requirements of the mixing vessels on the process plant thereby decreasing capital and operating costs. The benefit of using the dynamic optical flocculation monitor in combination with conventional UV_{254} absorbance removal was highlighted in this case, as the falsely high removal observed using 5.8 mg/l was clearly shown to be an unsuitable dose as the flocculation data showed that no detectable flocs formed.

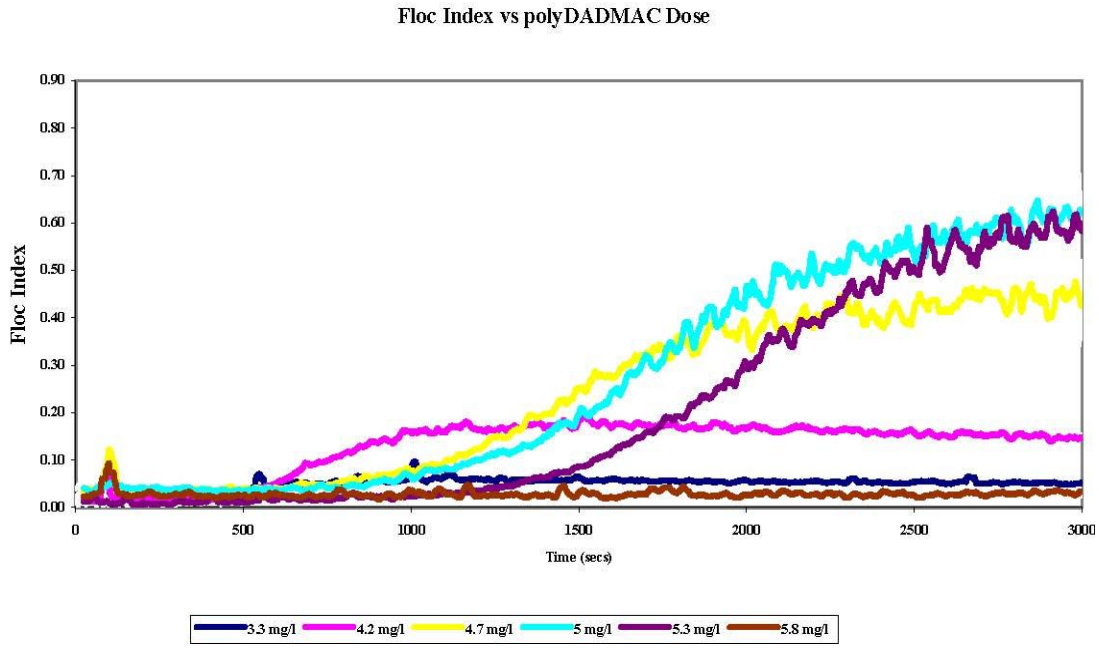


Figure 31 Flocculation curves obtained using polyDADMAC, pH 6.2, 22ºC (Raw water batch 2)

***Dose is expressed as mg/l active component of polyDADMAC**

Figure 32 shows the general trends between polyDADMAC dose, mean UV_{254} absorbance removal and mean dynamic flocculation parameters, RFI and FI_{max}. The best performing dose of polyDADMAC using raw water batch 2 and the dose range and conditions shown above would therefore be 5 mg/l. This dose removed 77% of the organic material (as measured by UV_{254} absorbance), giving a final UV_{254} reading of 6.5 abs/m, which was slightly higher than the industry standard of <5 abs/m. The dynamic flocculation parameter R_{FI} was again in agreement with the UV_{254} absorbance results, and showed that the dose of 5 mg/l formed the largest flocs in the fastest time. The inherent standard error of the UV spectrophotometer readings was found to be 0.9 abs/m. This suggests there was no significant difference in results between 3.3 mg/l and 4.2 mg/l. There was a significant improvement observed as the dose increased from 4.2 mg/l to 4.7 mg/l, but then performance according to UV_{254} absorbance was equivalent between the remaining doses.

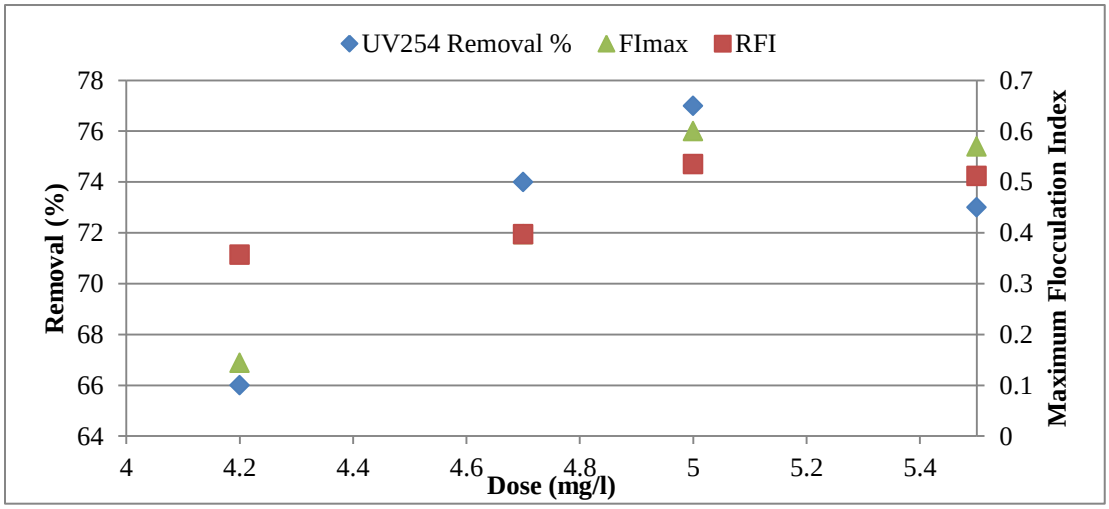


Figure 32 UV_{254} absorbance removal and dynamic flocculation parameters using polyDADMAC, pH 6.2, 22°C (Raw water batch 2)

Part 4.1.2 Coagulation and flocculation using Zetag 64 at pH 6.2

Zetag 64 is another cationic polymeric coagulant, with a slightly higher viscosity than polyDADMAC, lower charge density and a higher molecular weight. The same procedure as for polyDADMAC was followed. Gregory and Yukselen (2004) found that Zetag 64 produced very strong reversible floc and it was for this reason that it was evaluated in these tests on natural raw water. Figure 33 shows the UV_{254} absorbance removal profile with increasing dose

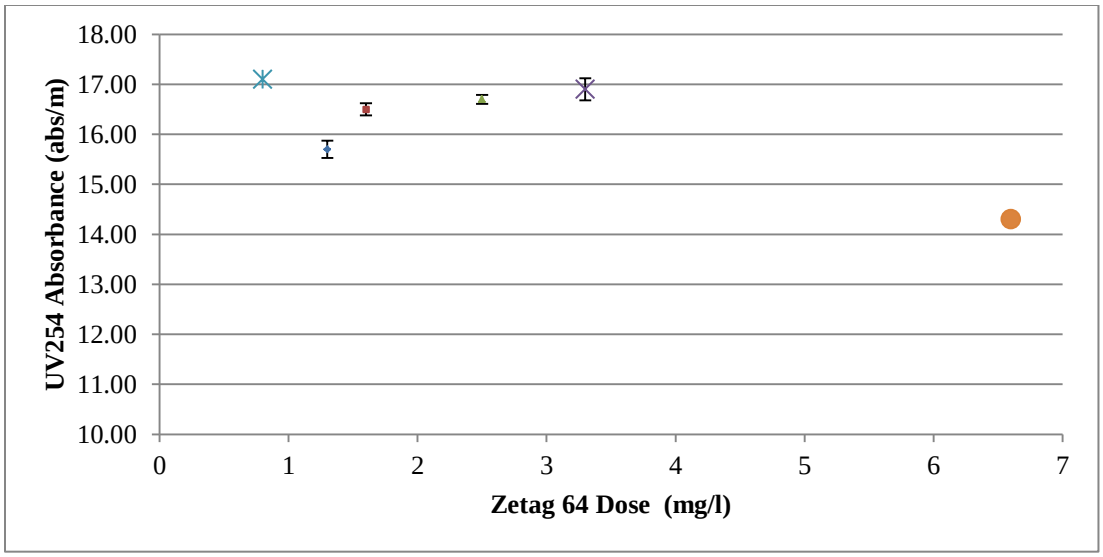


Figure 33 Residual UV_{254} absorbance using Zetag 64, pH 6.2, 22ºC (Raw water batch 2 – 30 abs/m)

The performance of Zetag 64 with respect to UV_{254} absorbance removal was very poor, with the best removal seen at 6.6 mg/l. This was a similarly erroneous result as seen with the highest dose of polyDADMAC as shown in figure 34 there was no detectable flocculation. This suggested that the UV_{254} absorbance removal was again misleadingly high as in the case seen with polyDADMAC. The dose with the highest UV_{254} absorbance removal and with detectable flocculation was therefore 1.3 mg/l with 49% removal.

The flocculation curves generated using 2.5 and 3.3 mg/l whilst showing some degree of flocculation, were sub-optimal in terms of flocculation rate. The residual UV_{254} absorbance using 1.3 mg/l was 15.7 abs/m, which would be unacceptable on a treatment plant as the risk of forming THM's would be too high and turbidity carryover would present too great a risk.

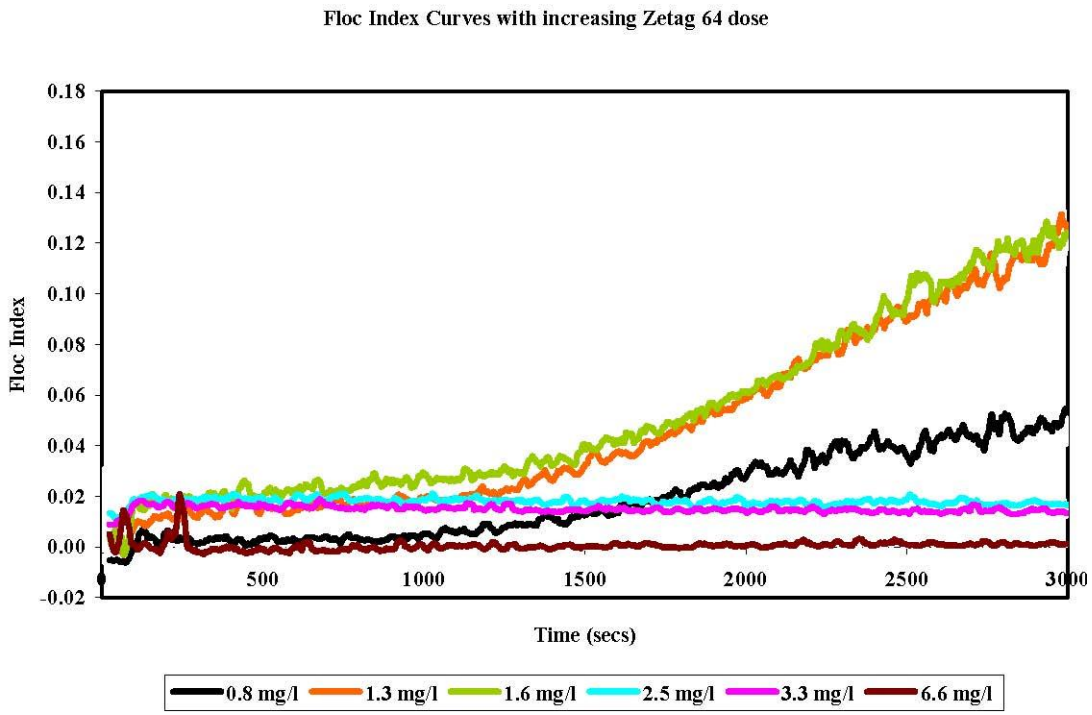


Figure 34 Dynamic flocculation curves using Zetag 64, pH 6.2 and 22ºC (Raw water batch 2)
Dose is expressed as mg/l active component of Zetag 64

The performance of Zetag 64 with respect to removal of UV_{254} absorbance was very poor and none of the doses used achieved the industry standard of <5 abs/m. The best removal was observed at a dose of 6.6 mg/l but this can be seen to have been misleading from figure 34, which shows that there was no detectable flocculation at this dose. This could be explained by the formation of a cationic humic complex, which was removed by the filtration through 0.45 membrane as seen in the case of the high polyDADMAC dose. This was the case for 2.5 mg/l, and 3.3 mg/l also as no detectable flocculation occurred but the UV_{254} absorbance removal was around 50% for both doses. The best dose out of the range used would therefore be 1.3 mg/l as this gave a removal of 49% and flocculation did occur, albeit to a smaller extent compared to ferric sulphate systems. Overall there was very little difference in the UV_{254} absorbance removal values for all doses and it was not possible to attain a viable dose. No further investigations were carried out with Zetag 64 as a sole primary coagulant.

The rate of flocculation was 100 times slower than polyDADMAC and the magnitude of FI_{max} was very small, both factors suggesting that the coagulation was poor. The doses that didn't achieve flocculation are not included in figure 35 as no curve-fitting could be applied to the data as no detectable flocculation occurred at these doses.

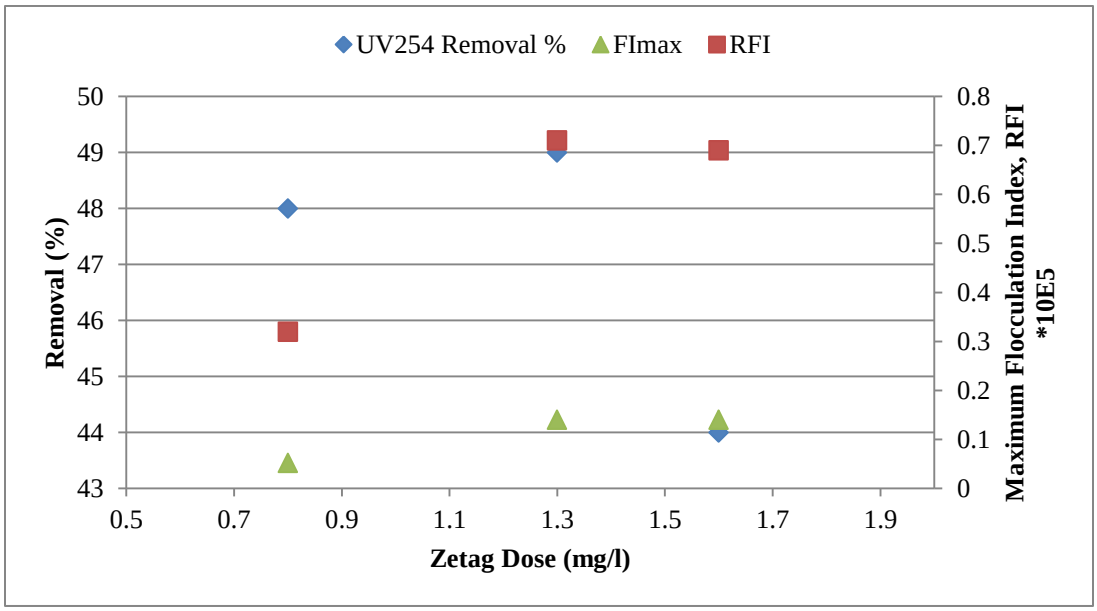


Figure 35 UV_{254} absorbance removal and dynamic flocculation parameters using Zetag 64, pH 6.2, 22ºC (Raw water batch 2)

Part 4.2 Coagulation and Flocculation using Combined Coagulant Systems at 22ºC

Part 4.2.0 Ferric sulphate and polyDADMAC at pH 4.5

It is known that hydrolysing metal salts produce weaker flocs than polymeric coagulants as has been shown by Jarvis *et al*. (2005), and the purpose of combining polymeric coagulants with ferric sulphate was to assess the effect of the combined coagulant system on UV_{254} absorbance removal and dynamic flocculation parameters. It was hoped that the combined coagulant system would have the benefits of increased floc strength due to the polymer along with the good removal of UV_{254} absorbance associated with ferric sulphate. The raw water used in these tests was taken from batch 3 which had a higher UV_{254} absorbance reading than the previous 2 batches.

This meant that the best doses established from the previous experiments wouldn't necessarily yield the same results with respect to UV_{254} absorbance as the previous experiments. It was decided that the ferric dose should be kept within the same range and the amount of organic coagulant varied, and the performance assessed. The previously determined optimum dose of 10.6 mg/l was used in these tests as it was desirable to under-dose ferric sulphate in order that the addition of the extra cationic additives wouldn't cause re-stabilisation of the colloidal material. It is common practice to reduce the ferric dose when combining with polymeric coagulants. Three doses of polyDADMAC were used based on the performance seen in the previous experiments and a dose of 10.6 mg/l ferric sulphate as Fe^{3+} was also used as a comparator. The UV_{254} absorbance removal trend is shown in figure 36.

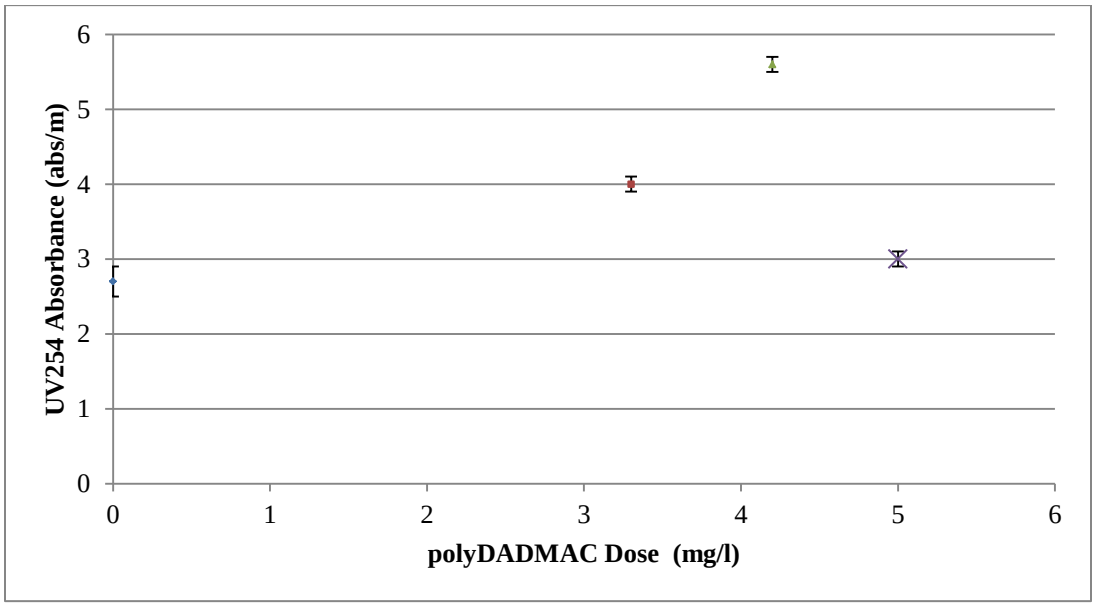


Figure 36 Residual UV_{254} Absorbance using 10.6 mg/l Ferric as Fe^{3+} and polyDADMAC, pH 4.5, 22 °C (Raw water batch 3 – 55 abs/m)

There appears to be little advantage gained from the addition of the polyDADMAC with respect to NOM removal, as the removal achieved with the dual coagulant system was less than that with ferric sulphate alone. It is interesting to note that the percentage removal with ferric alone was 95% compared to 98% for the previous water which was surprising considering that the raw water UV_{254} was 40% higher.

It was possible and indeed likely that the proportion of the hydrophobic and hydrophilic fraction may have been different in the 3rd raw water batch as this was known to have been collected after a heavy rainfall event. This may explain the seemingly small difference in removal compared to the large increase in raw water UV_{254} absorbance. This highlights the need to understand the chemical character of the NOM to ensure optimum dosing conditions that do not burden the downstream processes with unnecessary solids; as would happen if coagulant dose was tailored solely to UV_{254} absorbance. The combination of 10.6 mg/l ferric as Fe^{3+} and 5 mg/l polyDADMAC yielded reasonable results that were only marginally higher than with ferric alone. The flocculation curves shown in figure 37 further illustrate that there was no benefit from the addition of polyDADMAC. The coagulation process as measured by the PDA showed that the systems with dual coagulant produced detectable flocs at a slower rate, and these flocs were smaller than the system with ferric sulphate alone. It is also interesting to note that the dual coagulant systems all showed a decrease of approximately 15% in flocculation index after reaching $FI_{max.}$ This may indicate that the combination floc was not as strongly held together as the ferric floc as the ferric floc did not exhibit such a decrease in floc index during the flocculation part of the jar test.

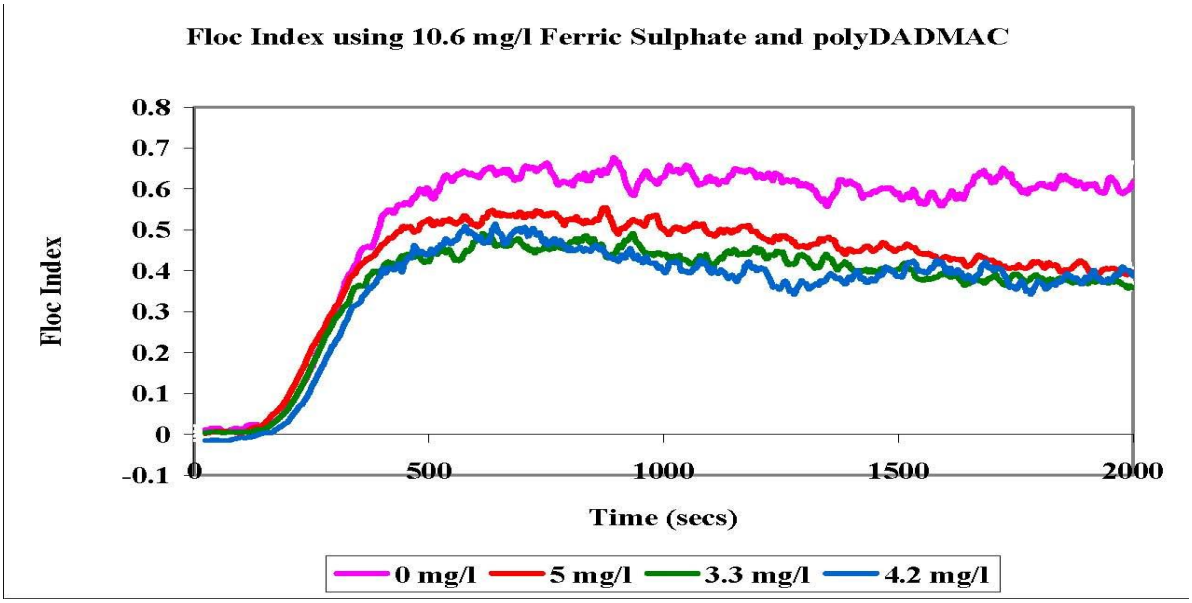


Figure 37 Dynamic flocculation curves using 10.6 mg/l ferric sulphate as Fe^{3+} and polyDADMAC (raw water batch 3). *Dose is expressed as mg/l as Fe^{3+}

Figure 38 shows a good correlation between the dynamic flocculation parameters and UV_{254} absorbance removal with all parameters indicating that the system with ferric sulphate alone was superior to the dual coagulant systems.

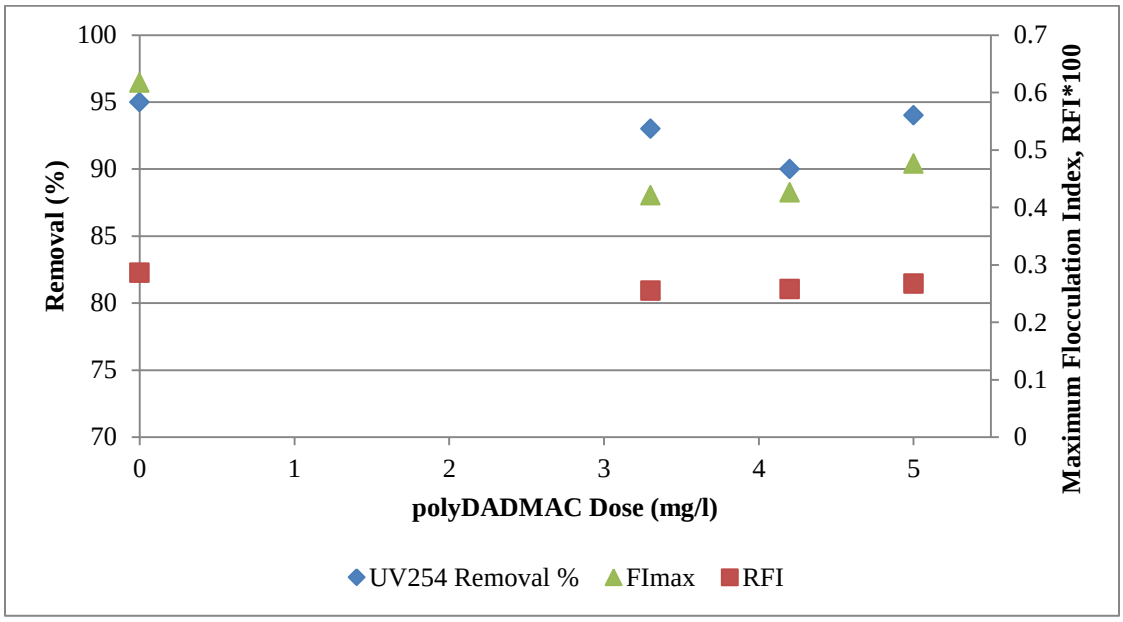


Figure 38 UV_{254} absorbance removal and dynamic flocculation parameters using 10.6 mg/l ferric sulphate as Fe^{3+} and polyDADMAC (Raw water batch 3)

This suggests that this dual coagulant system was not suitable for achieving a higher UV_{254} absorbance removal than ferric sulphate alone and coagulation performance wasn't optimal. The dual coagulant systems with the exception of 4.2 mg/l polyDADMAC were suitable with respect to removal of UV_{254} absorbance given the industry requirement of <5 abs/m. The best UV_{254} absorbance removal was obtained by using 5 mg/l polyDADMAC and this corresponded to the 2nd highest value of R_{FI} and FI_{max} and this system was used in the breakage tests detailed later in this section.

Part 4.2.1 Coagulation and flocculation using ferric sulphate and Zetag 64

The same principle was applied to these sets of experiments as for the previous ones and as the same batch of raw water was used it was decided that repeating the single ferric sulphate system was unnecessary and the original test would still be comparable.

The doses of Zetag 64 were decreased from the first test with Zetag 64 as trial tests showed that the doses used in the single coagulant test tended to form very large sticky flocs, which were too big for the PDA to read properly and derive flocculation curves from. Large sticky flocs wouldn't be desirable in a process situation as the filters would clog very fast so the doses were lowered using a trial and error method until this effect was minimised. The results are shown in figure 39.

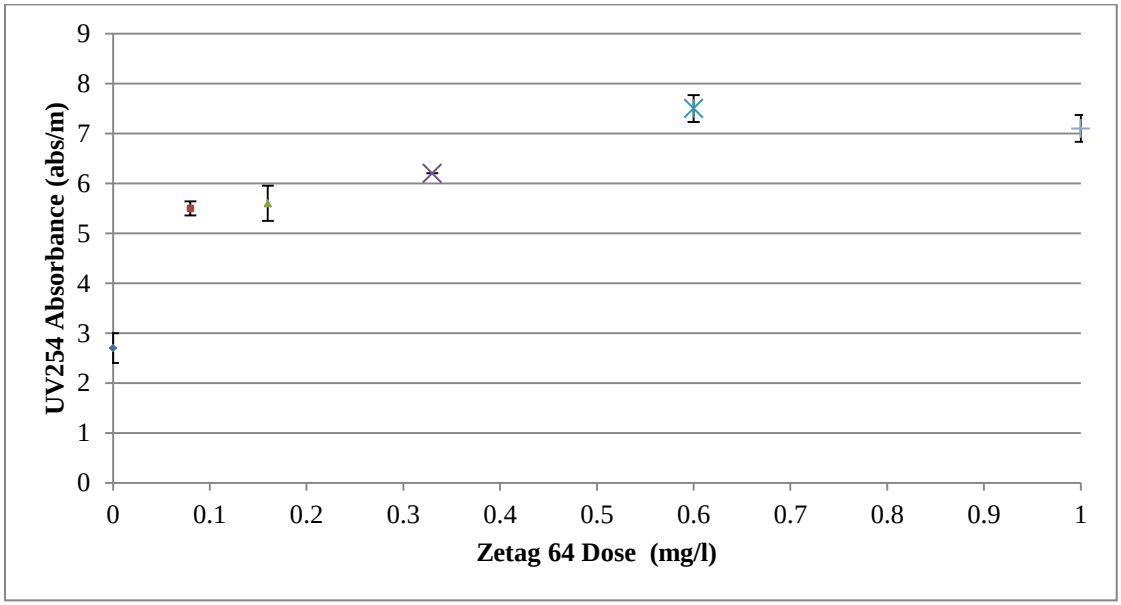


Figure 39 Residual UV_{254} absorbance using 10.6 mg/l Ferric as Fe^{3+} and Zetag 64 (Raw water batch 3)

The UV_{254} absorbance removal tended to decrease with increasing Zetag 64 dose, suggesting that the polymer inhibited the adsorption of ferric hydroxide complexes onto the humic substances by binding itself to the ferric hydroxide complexes. This seems likely considering the large sticky floc that formed with the larger doses of Zetag 64 and ferric used in the trial tests. It was likely that this situation was exacerbated by the order of addition of the coagulants. Addition of the polymer to the solution containing ferric/NOM micro-flocs seemed to have the effect of acting as a flocculant, ie: binding the existing aggregates together by bridging mechanisms. In this application the polymer's charge neutralisation ability was slightly impaired by the combination effect with the metal coagulant. The dual coagulant systems were all out of specification in this case with respect to achieving a residual UV_{254} absorbance of <5 abs/m.

Figure 40 shows that the flocculation performance was enhanced as the dose of Zetag 64 increased, with the largest flocs being formed the quickest with 1 mg/l of the polymer. This illustrates a situation where the dynamic flocculation parameter R_{FI} didn't correlate well with the removal performance ie: the fastest flocculating systems didn't perform the best in terms of NOM removal.

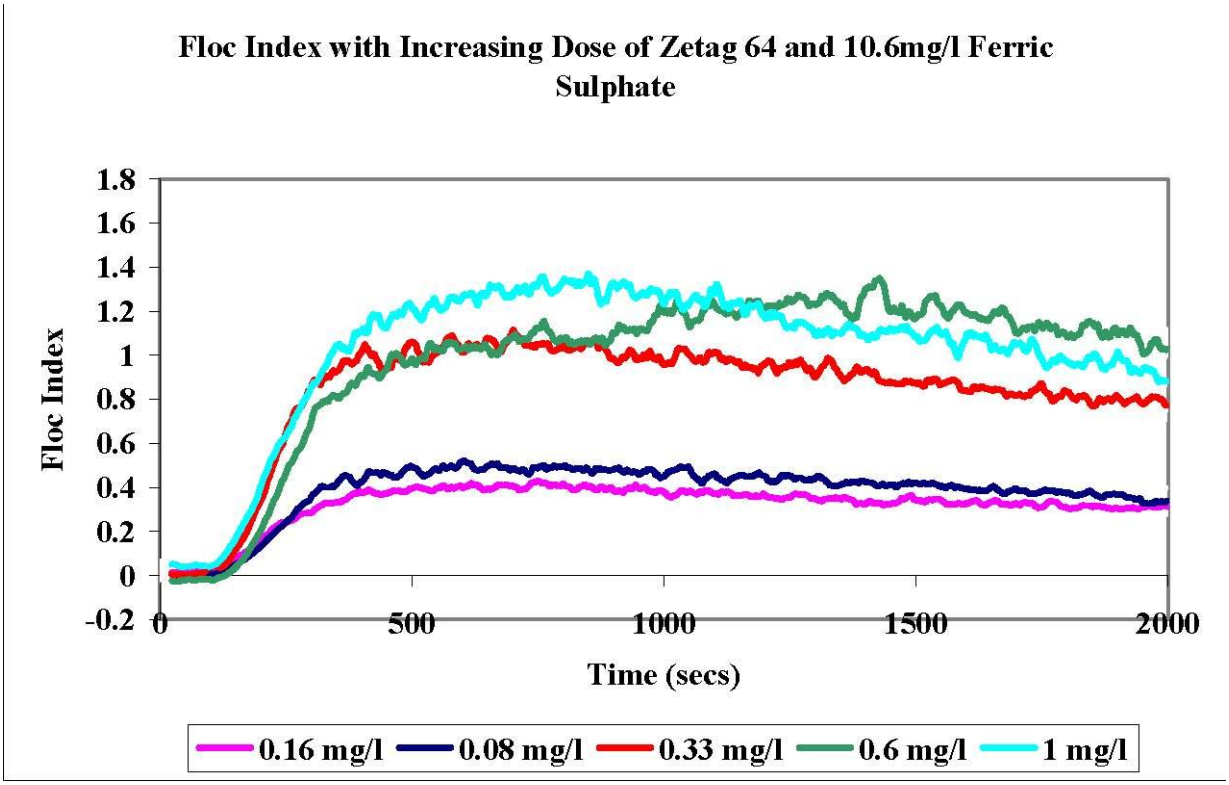


Figure 40 Dynamic flocculation curves using 10.6 mg/l ferric sulphate as Fe^{3+} and Zetag 64

All doses of Zetag 64 impaired the removal of humic substances as measured by UV_{254} absorbance but at least three of the doses (0.33 mg/l, 0.6 mg/l, 1mg/l) showed an increased FI_{max} and R_{FI} as shown in figure 41. Part of the Zetag 64 structure is comprised of acrylamide which is a well-known flocculant, and it is possible that the action of the polymer in this instance was more typical of a flocculant than a primary coagulant. The flocculant action in this case would be the formation of polymer bridges between the high molecular weight acrylamide chains.

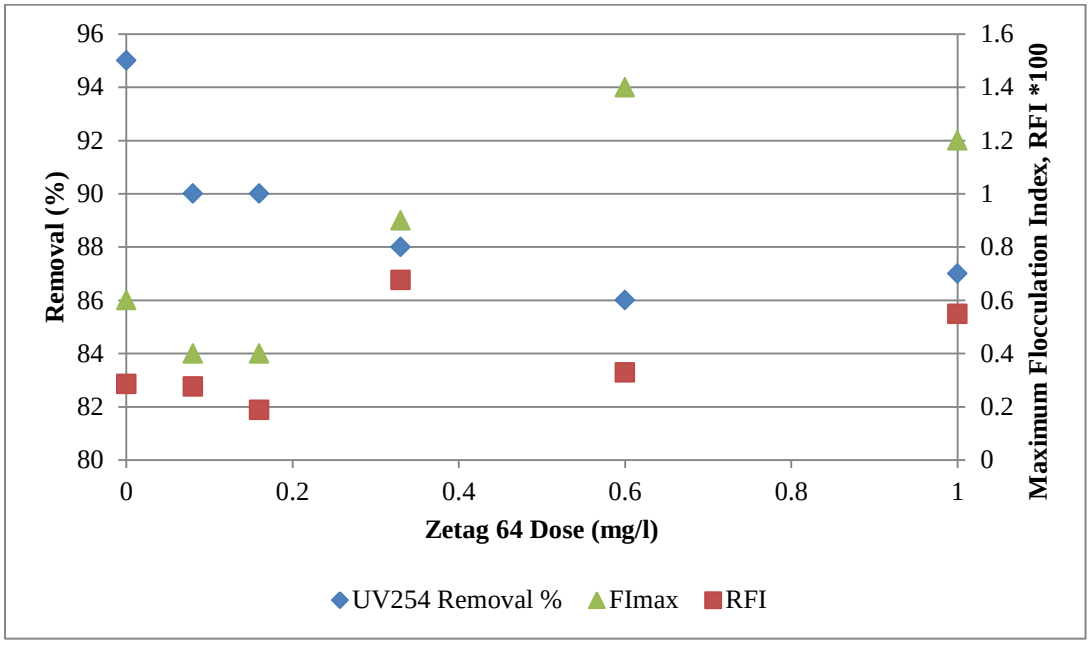


Figure 41 UV_{254} absorbance removal and dynamic flocculation parameters using 10.6 mg/l ferric sulphate as Fe^{3+} and Zetag 64 (Raw water batch 3)

Part 4.3 Comparison of coagulation and flocculation PDA results with single primary coagulants and dual coagulant systems

Tables 13 and 14 illustrate the jar test data in full. Comparisons between the single coagulant systems and the dual coagulant systems were difficult to make as it was clear that the water quality varied from one test to the other, but useful conclusions can be made from each test on its own and by use of UV_{254} absorbance removal parameter rather than residual. The parameters worth comparing were the rates of detectable flocculation (R_{FI}), the plateau values of the floc index curves (FI_{max}), and the removal of UV_{254} absorbance. It is worth noting that the purpose of the jar tests was to identify suitable doses of the coagulants in order to compare the floc properties of floc strength and reformation factor by means of breakage jar tests as detailed in Chapter 3. It was also useful to assess the relative merits of the different coagulant systems used.

System	Raw Water Batch No	Dose (mg/l)	UV_{254} raw (abs/m)	UV_{254} Residual test 1 (abs/m)	UV_{254} Residual test 2 (abs/m)	UV_{254} Residual test 3 (abs/m)	S.E Residual UV_{254}	Mean Residual UV_{254} (abs/m)	Mean UV_{254} removal (%)	R_{FI}	FI_{MAX} (Sigmoid fit)	r^2
1	1	3.5	28.7	10.5	10.3	10.9	0.18	10.6	63	0.00171	0.3	0.89
1	1	7.1	28.6	8.1	8.5	7.8	0.20	8.1	72	0.00171	0.3	0.88
1	1	10.6	28.7	0.45	0.51	0.51	0.02	0.5	98	0.00331	0.5	0.93
1	1	14.1	28.6	2.9	3.1	3.5	0.18	3.2	89	0.00251	0.4	0.92
1	3	10.6	55.1	2.5	2.5	3	0.17	2.7	95	0.00286	0.6	0.88
4	2	3.3	29	9.6	9.8	9.4	0.12	9.6	67	na	na	na
4	2	4.2	30.6	10	10.1	10.7	0.22	10.3	66	0.00036	0.1	0.93
4	2	4.7	28.7	7.5	7.5	7.5	0.00	7.5	74	0.0004	0.4	0.96
4	2	5	28.7	6.1	6.8	6.6	0.21	6.5	77	0.00054	0.6	0.97
4	2	5.5	27.2	6.9	7.2	7.6	0.20	7.2	73	0.00051	0.6	0.98
4	2	5.8	28.7	6.6	6.7	6.7	0.03	6.7	77	na	na	na
5	2	0.8	32.9	16.9	16.9	17.4	0.17	17.1	48	3.20E-05	0.1	0.89
5	2	1.3	30.8	15.5	15.6	15.9	0.12	15.7	49	7.10E-05	0.1	0.97
5	2	1.6	29.6	16.3	16.6	16.5	0.09	16.5	44	6.90E-05	0.1	0.96
5	2	2.5	32.9	16.9	17	16.3	0.22	16.7	49	na	na	na
5	2	3.3	32.9	17	16.8	16.9	0.06	16.9	49	na	na	na
5	2	6.6	30.8	14.1	14.1	14.6	0.17	14.3	54	na	na	na

Table 13 Jar test data using single primary coagulants

Key :System 1: Ferric sulphate System 4: polyDADMAC System 5: Zetag 64

System	Raw Water Batch No	Dose (mg/l)	UV_{254} raw (abs/m)	UV_{254} Residual test 1 (abs/m)	UV_{254} Residual test 2 (abs/m)	UV_{254} Residual test 3 (abs/m)	S.E Residual UV_{254}	Mean Residual UV_{254} (abs/m)	Mean UV_{254} removal (%)	R_{FI}	FI_{MAX} (Sigmoid fit)	r^2
2	3	3.3	55.1	3.8	3.9	4.3	0.15	4	93	0.00255	0.4	0.92
2	3	4.2	55.1	5.5	5.5	5.8	0.10	5.6	90	0.00258	0.4	0.96
2	3	5	55.1	3.2	3	2.9	0.09	3	94	0.00267	0.5	0.91
3	3	0.08	53.9	5.5	5.2	5.7	0.14	5.5	90	0.00276	0.4	0.85
3	3	0.16	53.9	4.9	6	5.9	0.35	5.6	90	0.00188	0.4	0.86
3	3	0.33	53.9	6.2	6.2	6.2	0.00	6.2	88	0.00676	0.9	0.88
3	3	0.6	53.9	7	7.6	7.9	0.27	7.5	86	0.00329	1.4	0.93
3	3	1	53.9	7.2	7.5	6.6	0.27	7.1	87	0.00549	1.2	0.85

Table 14 Jar test data using dual coagulant systems with 10.6 mg/l ferric sulphate as Fe^{3+} and cationic polymeric additives

Key: System 2: 10.6 mg/l ferric sulphate and polyDADMAC System 3: 10.6 mg/l ferric sulphate and Zetag 64

The regression coefficient r^2 values showed a good fit of the Sigmoid curve to the data, with values of 0.85 and over in all cases where there was visible flocculation. This justified the use of the Sigmoid function to obtain the gradient of the flocculation index curve at its maximum point and the maximum FI_{max} using Tablecurve$_{TM}$. Figure 42 shows the UV_{254} absorbance removal of the single coagulant systems, based on the best removal and the fastest flocculation rate.

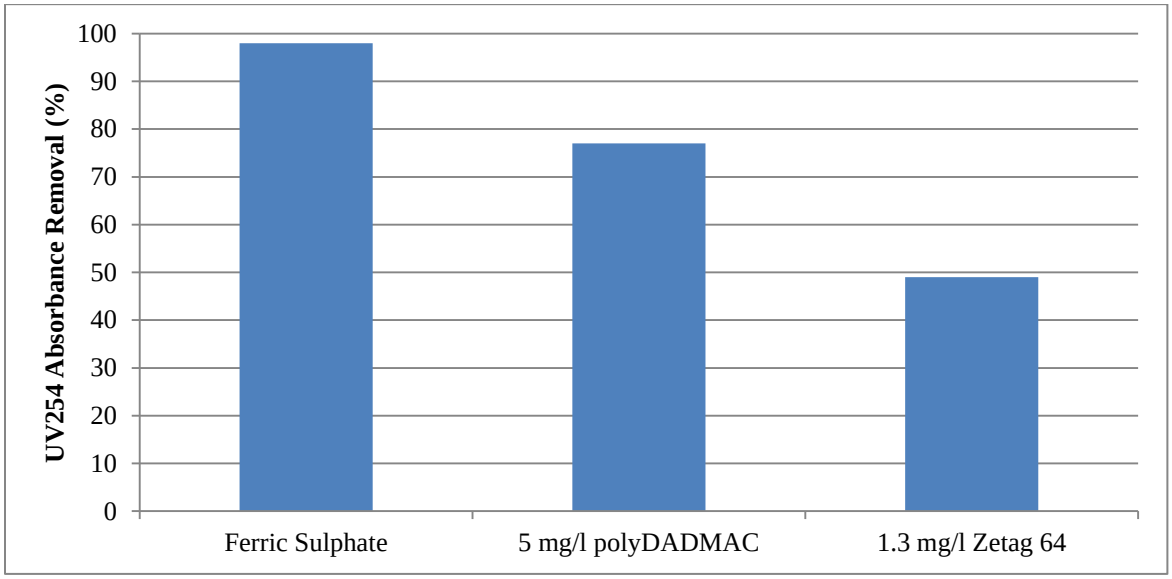


Figure 42 UV_{254} Absorbance removal using ferric sulphate, 5 mg/l polyDADMAC and 1.3 mg/l Zetag 64 (raw water batches 1 and 2)

Of the systems used, ferric sulphate was the best coagulant for removing the UV_{254} absorbing compounds, the final water UV_{254}absorbance reading were considerably less than the industry requirement of <5 abs/m using the two cationic polymers. The system using polyDADMAC didn't perform well, and this has been noted before. Bolto *et al.* (1999) found that both medium and high molecular weight polyDADMAC performed less well for removing UV_{254} absorbing compounds on three different reconstituted natural water sources when compared to alum. The final water UV_{254} absorbance using polyDADMAC was not far in excess of 5 abs/m, at an average of 6.5 abs/m but would still present and unacceptable risk with respect to THM formation potential. The best removal recorded with Zetag 64 was far below an acceptable quality, and it has to be concluded that this coagulant was not very effective at treating the raw water used with the dose range tested.

The dynamic flocculation data corresponded well with the observations from Gregory and Nelson (1986) and Gregory and Kam (2001), that the speed of particle aggregation is indicative of the coagulation performance. It was noted that the value of R_{FI} was largest for the systems with the best UV_{254} absorbance removal. The flocculation rate observed using the best dose for UV_{254} absorbance removal was found to be in the order:

R_{FI} ferric sulphate> R_{FI} polyDADMAC> R_{FI} Zetag 64

This also confirmed the usefulness of the PDA and the dynamic flocculation data that can be generated. The magnitudes of R_{FI} showed that the values for ferric sulphate were 10 times higher than those with polyDADMAC and Zetag 64. The time taken for flocculation to be detected was also considerably longer with the polymeric additives. The data yielded from the PDA with respect to flocculation rate could with the benefit of more repeats be used at the initial design stage of plant flocculator units provided the hydraulic conditions could be scaled down successfully. Figure 43 shows the UV_{254} absorbance removal percentages for the dual coagulant systems compared with ferric sulphate only.

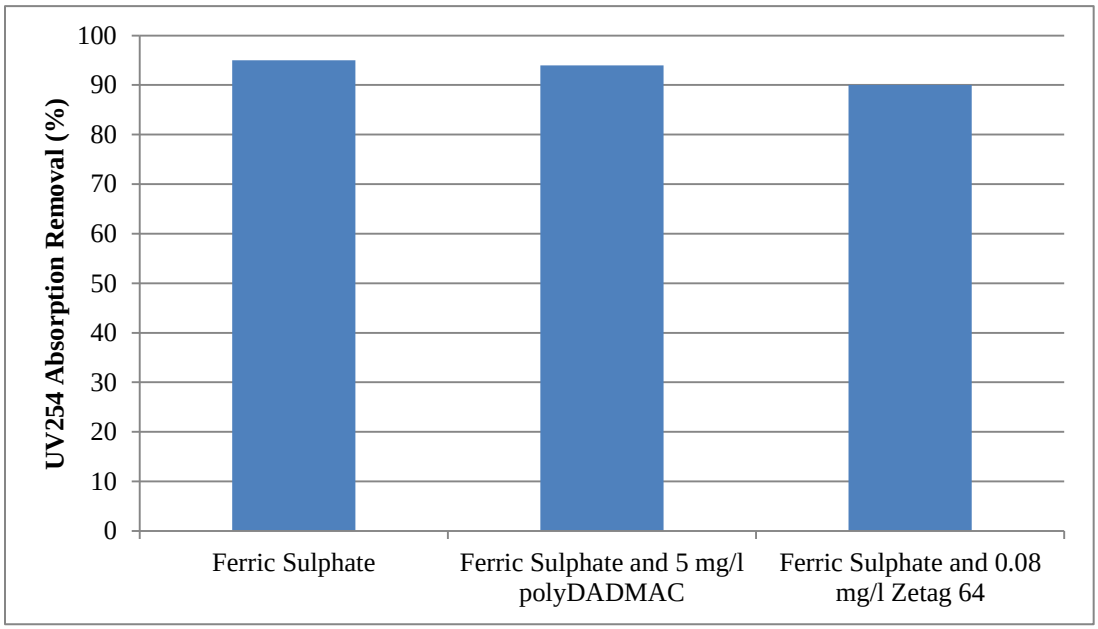


Figure 43 UV_{254} absorbance removal using 10.6 mg/l ferric sulphate as Fe^{3+} combined with cationic polymeric additives (raw water batch 3)

The system with the best UV_{254} absorbance removal was ferric sulphate, and very closely followed by ferric sulphate and polyDADMAC, and finally ferric sulphate and Zetag 64. The residual levels of UV_{254} absorbance were 2.7, 3, and 5.5 abs/m respectively. Realistically the differences in NOM removal between the first two systems (95% and 94% respectively) were minimal and all systems showed reasonably good performance in terms of removal of humic substances. The dynamic flocculation data showed that the fastest growing and largest flocs were generated from the combination of ferric sulphate and Zetag 64 but the corresponding UV_{254} absorbance was slightly worse than with ferric sulphate alone. The degree of UV_{254} absorbance removal didn't vary to a great extent between the doses of Zetag 64 suggesting that there was no significant difference in performance as dose increased. The dynamic flocculation data showed very big differences between the doses, but with no discernible relationship between dose and R_{FI} and dose and FI_{max}. This suggests that the mechanism of coagulation and flocculation with this particular polymer was different when combined with Ferric sulphate.

It was noted in trial tests, that higher doses of Zetag 64 (>1.5 mg/l) produced very large sticky floc almost instantaneously after addition of the two coagulants to the raw water. These flocs were too large to be detected by the PDA accurately and therefore the dose was lowered for the breakage jar tests. This suggests that some reaction between the coagulants occurred as they were added simultaneously, which reduced the potential of the ferric to adsorb onto the humic acid, consequently reducing the UV_{254} absorbance removal capability. The reason for the formation of very large flocs can be explained by bridging reactions between the polymer chains, which is a common phenomenon frequently reported with polymeric coagulants. As mentioned previously part of the Zetag 64 structure is comprised of acrylamide which is a well-known and widely used flocculant and it is likely that the polymer has acted in this way in the jar tests utilising the combination of ferric and Zetag 64.

The dual coagulant system with ferric sulphate and polyDADMAC showed very little difference in UV_{254} absorbance removal or RFI between the doses of polyDADMAC. The jar tests using polyDADMAC on its own showed that the rate of flocculation was very slow compared to Ferric sulphate, it appears that there was no benefit to adding the polymer in this instance as the de-stabilisation was already carried out by the ferric sulphate.

Part 4.4 Breakage jar tests using single coagulant systems at 22ºC

The objective of the breakage jar tests was to quantify the strength and reformation capability of floc created with each of the coagulant systems used in the previous jar test; having established a suitable dose from the previous test results. The breakage jar tests were carried out after each jar test, and on the same raw water. The UV_{254} absorbance was not measured in this case as it was thought that the breakage jar test conditions would have no influence on the removal capability, therefore the removal was assumed to be the same as for the normal jar tests. The four systems and doses used were as follows:

1. Ferric sulphate 10.6 mg/l (raw batch 1)
2. polyDADMAC 5 mg/l (raw batch 2)
3. Ferric sulphate 10.6 mg/l and 0.08 mg/l Zetag 64 (raw batch 3)
4. Ferric sulphate 10.6 mg/l and 5 mg/l polyDADMAC (raw batch 3)

The floc strength and reformation ability is quantified in this research by calculation of two ratios as described in Chapter 3, these are:

- Floc Strength factor – FI_{break}/FI_{max}
- Reformation factor – $(FI_{ref} - FI_{break})/(FI_{max}-FI_{break})$

The values of the two factors were calculated using the data taken from the Tablecurve^{TM} package after fitting the flocculation index data to the Sigmoid function. The shape of the dynamic flocculation curves generated by the breakage jar test were modelled as two distinct Sigmoid curves as detailed in Chapter 3, and the data was split into the 1st phase of floc growth and the 2nd phase of floc re-growth.

Part 4.4.0 Breakage Jar Tests using ferric sulphate

Figure 44 shows the dynamic flocculation data from the breakage jar test, the onset of the rapid mix period is quite clearly defined by a sharp decrease in floc index at around 1000 seconds into the test. The slight increase at the onset of the rapid mix was due to air bubbles being caught in the sample line. The degree of floc breakage that occurred during the second rapid mix period was high, which suggested that the floc formed with ferric sulphate was weak in structure and unable to resist the increased shear forces imparted during the rapid mix phase. The floc strength and reformation figures are not absolute values with a specific reference point, and are best utilised by comparison between the systems which will be included later in this section. The floc strength factor as shown in table 10, was 0.34 and the reformation factor 0.1 which showed that the floc was unable to maintain its structure during increased shear, and showed very poor reformation ability when original stirring conditions were returned. The initial data suggests that the floc was weak as the floc was broken as the stirring speed increased, and once broken was unable to reform. This type of irreversibility has been seen before with hydrolysing metal coagulants (Gregory and Yukselen, 2002).

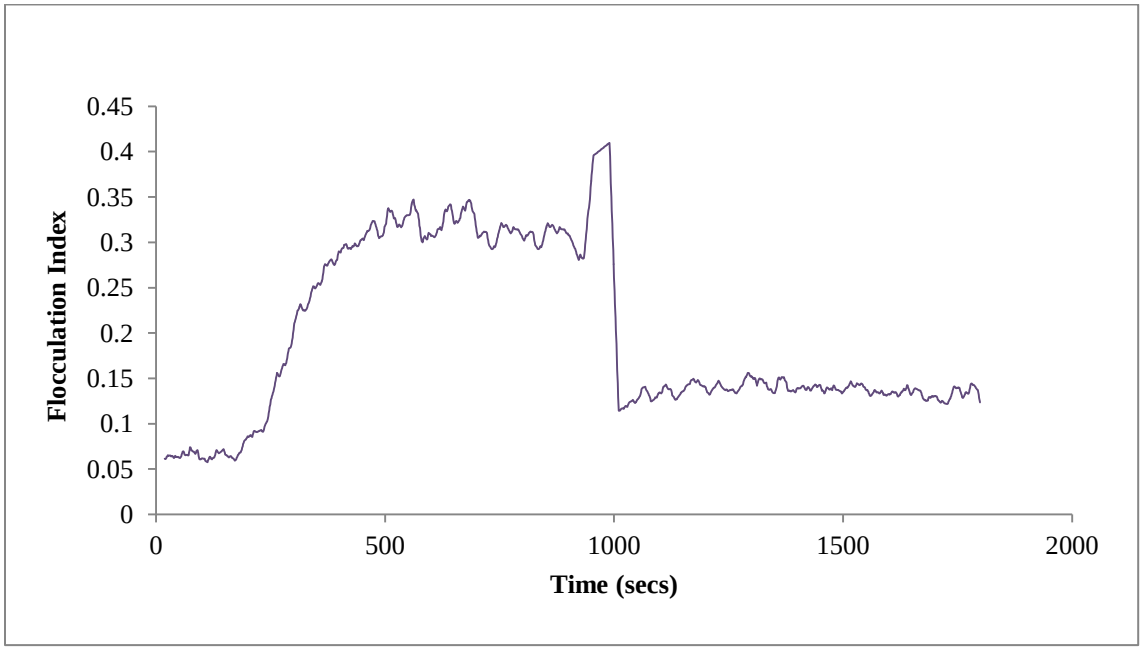


Figure 44 Floc Growth, Breakage and Reformation using 10.6 mg/l ferric sulphate as Fe^{3+}(raw water batch 1)

Figure 45 illustrates a very different floc growth curve to that seen with ferric sulphate, as the period of floc growth was much slower as was observed in the jar tests, but the degree of reformation was considerably higher and may have achieved complete reversibility if the test had continued for a longer duration. The floc was broken down to a similar extent after the rapid mix period as with ferric sulphate, but the re-growth was almost fully reversible. The floc strength factor was low at 0.08, but the reformation factor was high at 0.7, which suggested that the floc formed was weak in the sense of not being resistant to shear but capable of good reformation when the original stirring conditions were returned. This appears to be the reverse of that seen in the previous breakage test using ferric sulphate.

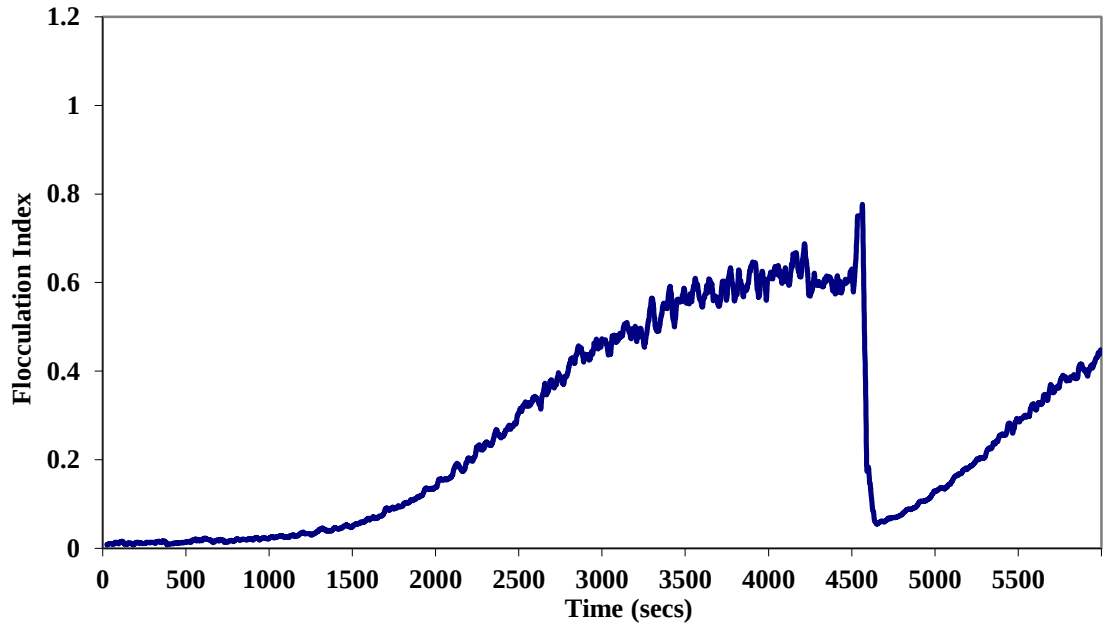


Figure 45 Floc growth, breakage and reformation using 5 mg/l polyDADMAC (raw water batch 2)

Part 4.4.1 Ferric sulphate and polyDADMAC

Figure 46 shows that the floc re-growth after the rapid mix period was not fully reversible, as was the case with ferric sulphate on its own. The floc strength and reformation factors were similarly low at 0.29 and 0.32 respectively. It was evident from the previous jar tests using polyDADMAC and ferric sulphate that the addition of polyDADMAC had no beneficial effect on the UV_{254} absorbance removal, and figure 45 shows that there was no benefit with respect to floc strength factor but there was an increase in reformation factor. As the polyDADMAC took a very long time to form aggregates during the test as a single primary coagulant, it is logical to postulate that in combination with the much faster reacting ferric sulphate; the polymer was left to interact with ferric/humic floc rather than humic substances and therefore was acting as a flocculant rather than a coagulant.

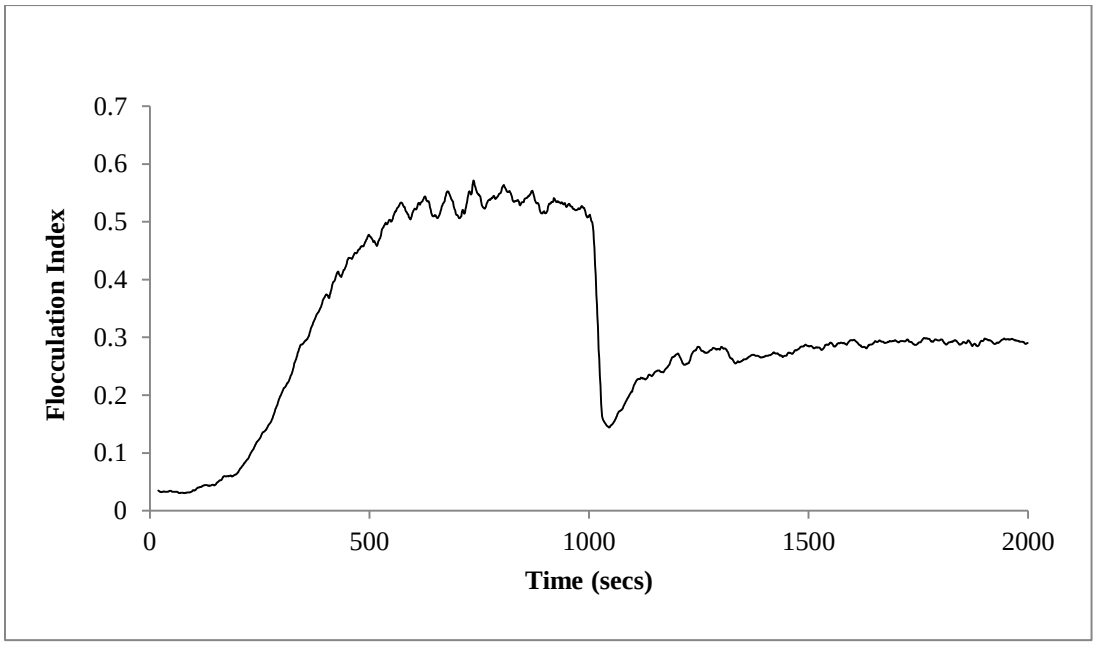


Figure 46 Floc growth, breakage and reformation using 10.6 mg/l ferric sulphate as Fe^{3+} and 5 mg/l polyDADMAC (raw water batch 3)

Part 4.4.2 Ferric sulphate and Zetag 64

Figure 47 showed an improved amount of floc reformation after the rapid mix period compared to ferric sulphate, and ferric sulphate and polyDADMAC. The floc strength factor was 0.24 and the floc reformation factor higher was 0.43. The floc strength factor was similar to the 2 other ferric sulphate based systems, but there was a notable improvement in floc reformation capability. This supports the supposition that the Zetag 64 was not acting as a coagulant, and was acting more like a flocculant thereby increasing the reformation ability.

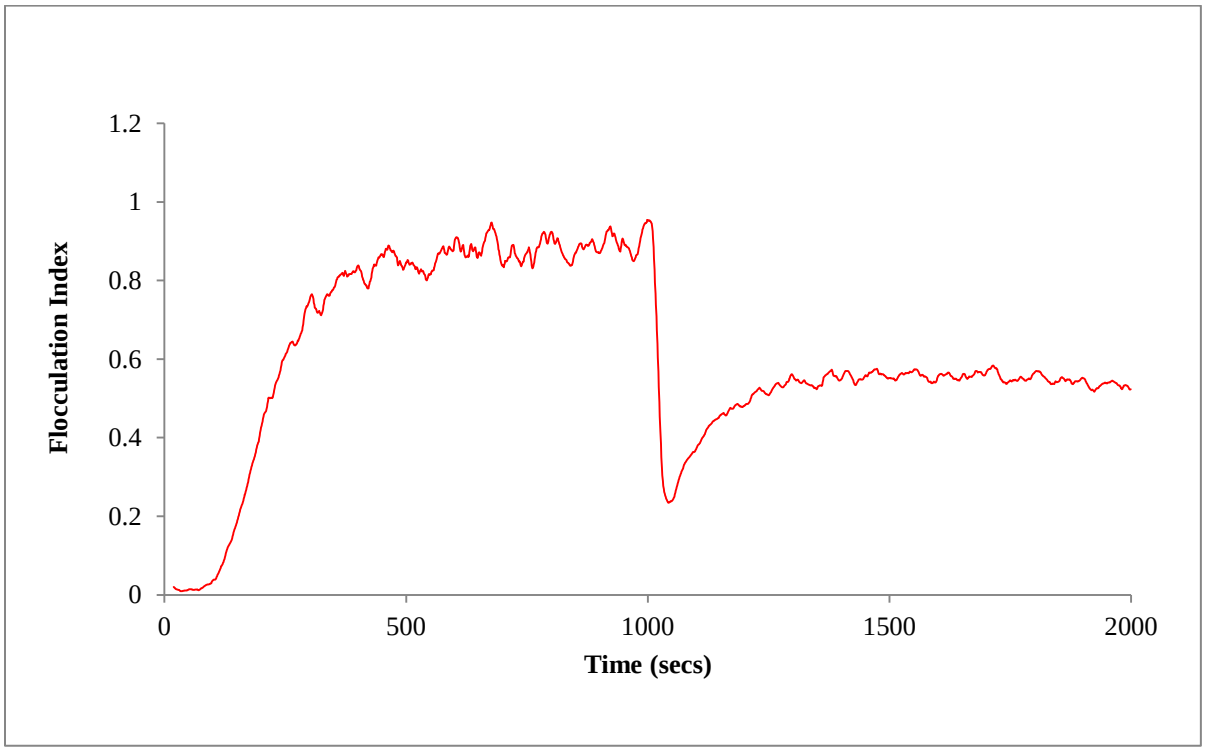


Figure 47 Floc growth, breakage and reformation using 10.6 mg/l ferric sulphate as Fe^{3+} and 0.08 mg/l Zetag 64 (raw water batch 3)

Part 4.4.3 Summary of dual coagulant system performance

A comparison of the dual coagulant systems with ferric sulphate is shown in figure 48, it is clear that the different systems gave rise to different size flocs before, during and after the rapid mix period. The dual coagulant systems exhibited higher floc reformation values than with ferric sulphate alone. During the jar tests, the UV_{254} absorbance removal between the three systems was very similar with the best removal seen with ferric sulphate alone. However, the systems with the dual coagulants showed improved reformation performance that could make up for their slightly poorer UV_{254} absorbance removal, if generation of a more reversible floc was more desirable than achieving the best residual UV_{254} absorbance. It is worth noting at this point that raw water batch 3 which was used with both dual coagulant systems was higher in NOM content than batches 1 and 2. The ferric sulphate breakage test was carried out with batch 1 and therefore, this dose may not have been high enough to remove the maximum NOM. However the removal with 10.6 mg/l ferric sulphate as Fe^{3+}on batch 3 was still 95%, rather than 98% which suggests the comparison is still valid – and t-Test p value from comparison of the removal data sets was >0.05 thereby implying that the difference in removal wasn't significant.

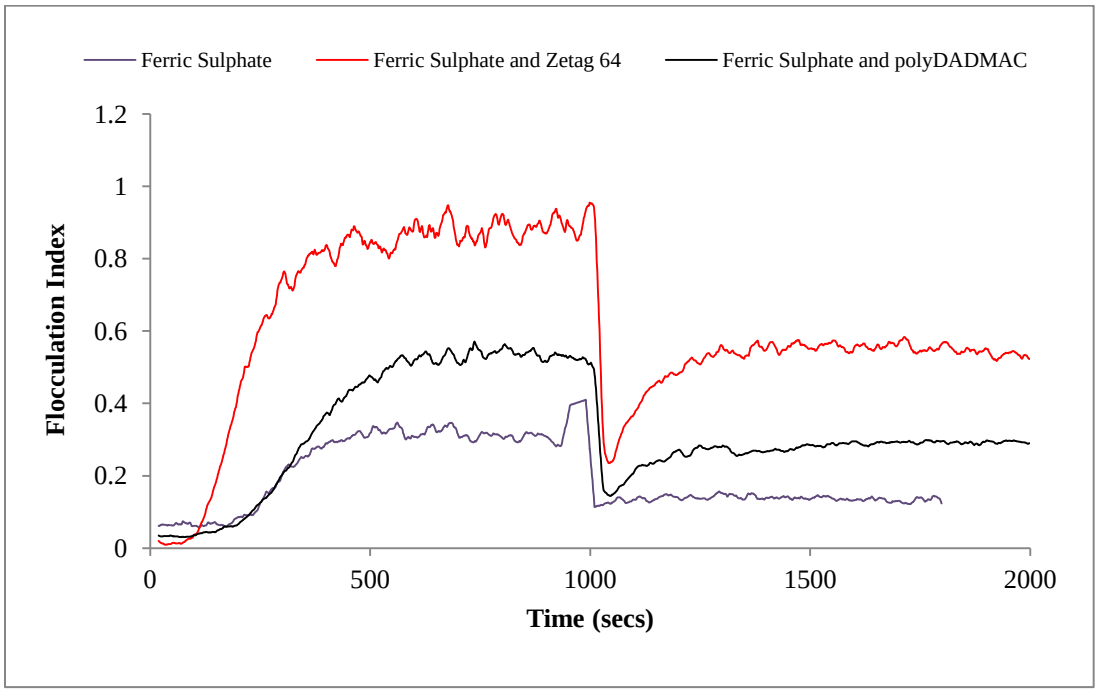


Figure 48 Floc growth, breakage and reformation using 10.6 mg/l ferric sulphate as Fe^{3+} in combination with cationic polymeric additives

Figure 49 shows the relationship between the maximum floc size, and floc strength factor and floc reformation factor for the ferric sulphate based systems. Figure 49 shows that floc reformation factor increased with floc size, and the reverse was true with floc strength factor. This is an interesting trend, as it would be logical to expect that larger floc would correspond with stronger floc as the flocs have been subjected to the same shear field in each test so it should be the case that flocs that have grown to a larger size, should be stronger. The compactness of the floc structure is likely to play a part in this aspect, if as postulated earlier; the two polymeric additives were acting more as flocculants and therefore were forming larger and more open floc structures than with ferric alone which may have been more compact. A larger and more open floc structure would therefore not be as strong as a small, compact structure comparative to its size. The difference between the FI_{max} values and the FI_{break} values support the mechanism of floc fragmentation in the ferric sulphate system as the flocculation index values decreased down to very low levels (Yu *et al*., 2010). Conversely the higher values of FI_{break} obtained using the dual coagulant systems are more supportive of the mechanism of surface erosion. This is discussed further in Chapter 8.

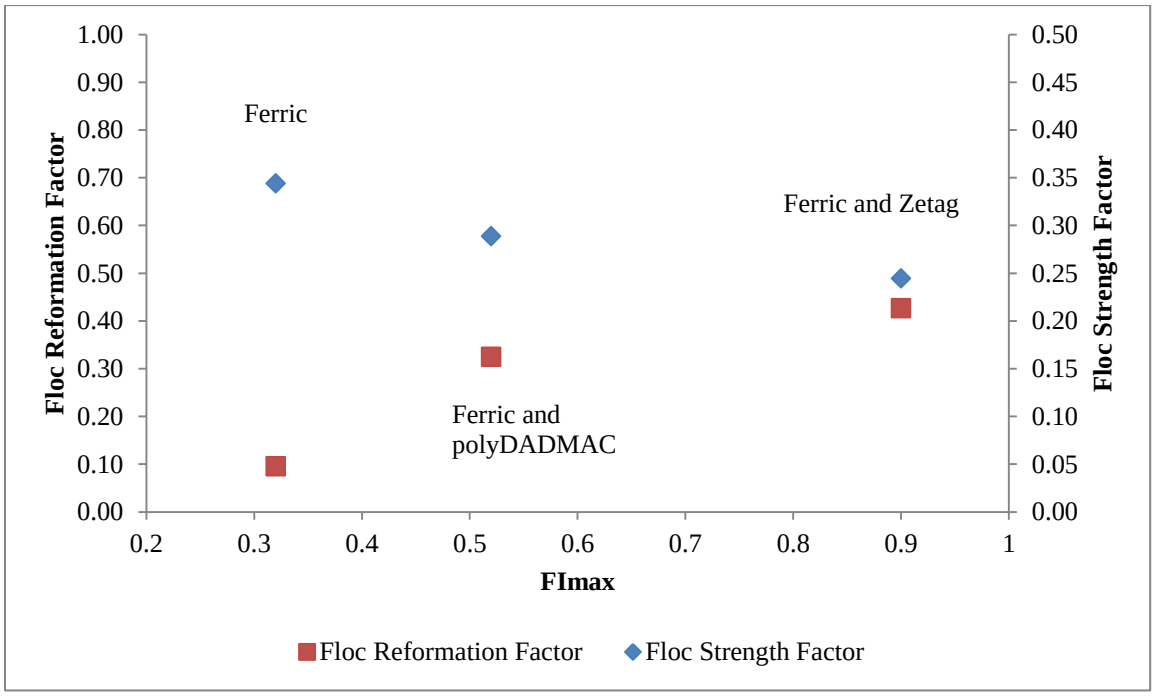


Figure 49 Floc size and floc strength factor and floc reformation factor using ferric sulphate based coagulant systems

Table 15 gives a summary of the mean dynamic flocculation parameters generated from the breakage jar tests.

Coagulant System	Raw Water Batch Number	UV_{254} Absorbance Removal (%)*	FI_{max}	FI_{break}	FI_{ref}	Floc Strength Factor	Floc Reformation Factor
10.6 mg/l Ferric Sulphate	1	98	0.32	0.11	0.13	0.34	0.10
10.6 mg/l Ferric sulphate and 5 mg/l polyDADMAC	3	94	0.52	0.15	0.27	0.29	0.32
10.6 mg/l Ferric sulphate and 0.08 mg/l Zetag 64	3	90	0.9	0.22	0.51	0.24	0.43
5 mg/l polyDADMAC	2	77	0.62	0.05	0.45	0.08	0.70

Table 15 Summary of mean dynamic flocculation parameters using ferric sulphate and cationic polymeric additives

* UV_{254} absorbance figures taken from the mean of the jar test results.

Part 4.6 Results summary

Overall the jar tests carried out in this initial study into the effects of coagulant type on floc properties and NOM removal have shown some interesting results that have implications for the experimental work programme in this project. The raw water quality data showed that over the 2 month period of March-April 2002, there was some variability in NOM content but reasonable consistency in terms of pH and turbidity. This was expected and so future experiments need to continue to include raw water quality in terms of NOM content. The third batch of raw water was significantly different in terms of NOM content, and in hindsight it would have been preferable to perform the optimum dose tests on batch 3 again to ascertain the optimum dose of ferric sulphate, and then decide the polymer doses. The flocculation rate or R_{FI} was found to correlate well with NOM removal in the systems where charge-neutralisation was deemed to be the main removal mechanism, but less well in the combined system of ferric sulphate and Zetag 64.

The reason for this is thought to be due to the polymer bridging effects between the acrylamide parts of the polymer. The doses trialled at >1.5 mg/l and 10.6 mg/l ferric sulphate as Fe^{3+} produced very large and "sticky" floc within a very short period of time – which wasn't consistent with the long slow adsorption times observed when using Zetag 64 as a primary coagulant presumably by charge neutralisation. This supports the concept of Zetag 64 acting as a flocculant when added in combination with ferric sulphate. Measurements of surface charge would have been beneficial in understanding the mechanism of the coagulant systems better, in particular those with the combined coagulants. Comparisons between the five coagulant systems showed that with the exception of 5 mg/l polyDADMAC and the combined system of ferric sulphate and Zetag 64; all systems were significantly different with respect to NOM removal. The best performing coagulant systems for NOM removal was ferric sulphate on its own. The polymeric additives were not found to improve NOM removal, but the breakage test results indicated that the floc formed with the combined coagulant systems behaved differently during, and after the breakage period. The flocs formed with ferric sulphate were comparatively smaller, more resistant to shear relative to their size, but less reversible.

Conversely the combined coagulant systems and 5 mg/l polyDADMAC formed comparatively larger floc that was less resistant to shear, but was more reversibly formed. The reason for the formation of the larger floc in the case of the combined system with Zetag 64 was thought to be due to polymer bridging between the acrylamide parts of the polymer giving rise to larger more open floc structures. The mode of action of the polyDADMAC in combination with the ferric sulphate was thought to be due to be a combination of "electrostatic patch" effects as reported by Gregory (1996) by interaction of polyDADMAC with NOM and conventional charge-neutralisation with ferric sulphate. Polymer bridging was disregarded as a potential mechanism of the polyDADMAC combination system as high charge density compounds such as polyDADMAC tend to adopt flat configurations which minimise bridging potential (Bolto and Gregory, 2007).

The five coagulant systems were tested by means of conventional jar tests, and breakage jar tests and the overall performance in terms of both NOM removal and floc properties formulated the next stage of experimental work. The NOM removal was comparatively superior with ferric sulphate using raw water batch 1, and slightly better using raw water batch 3. The floc strength factor was highest when using ferric sulphate alone, but the floc size and reformation was lowest. Realistically NOM removal is one of the key parameters driving treatment of high NOM water and any dual coagulant system used on a full-scale plant would have to show both improved floc strength and reformation properties and good UV_{254} absorbance removal performance. It is interesting to note that the two objectives may not always converge. The dual coagulant systems were not tested further due to the above points regarding their decreased NOM removal, and the polymeric additives were not pursued due to their long adsorption times which would not be possible to account for on the DA20 pilot plant.

Part 4.7 Conclusions

The following key points can be concluded from the UCL based jar tests:

- The PDA produced reproducible flocculation curves and can therefore continue to be used in this project.
- The polymeric additives used as sole coagulants took considerable longer to form floc, and in the case of polyDADMAC produced more reversible floc but with comparatively poor NOM removal.
- Zetag 64 on its own showed very poor removal of NOM, which was attributed to the very slow rate of adsorption and subsequent flocculation. This meant that the transport and attachment of the polymer onto the humic substances must have been impaired in some manner, perhaps by steric repulsion effects.
- The removal of UV_{254} absorbing compounds was best using ferric sulphate alone, and the floc strength factor for this system was highest, but the floc reformation factor was lowest.

- Floc reformation improved by the combination of ferric sulphate with the polymeric additives, but strength factor decreased as did NOM removal. This is thought to be due to the polymeric additives acting more as flocculants than coagulants.
- The system with ferric sulphate and Zetag 64 showed evidence of surface erosion breakage mode as FI_{break} values were comparatively higher.
- The systems with ferric sulphate, and ferric sulphate and polyDADMAC showed evidence of the fragmentation breakage mode as FI_{break} was comparatively smaller than with ferric sulphate and Zetag 64.

Overall it was concluded that although the polymeric additives had beneficial effects on the reversibility of the floc after breakage compared to ferric sulphate, but the NOM removal was not good enough to warrant continued investigation. The resistance to breakage was also lower with the polymeric additive systems, which would not be beneficial with respect to improving the robustness of the floc at Albert WTW. The experimental focus then moved onto exploring the properties of ferric based systems by changing parameters such as coagulation pH and ferric dose ratio to NOM content.

Chapter 5 The effect of coagulation pH and Fe:DOC ratio on floc properties and NOM removal

Part 5.0 Introduction

The previous set of jar tests presented in chapter 4 showed that with the ferric sulphate system, the maximum floc size and flocculation rate were affected by the dose and also correlated well with NOM removal; but the relative impacts of the dose on the floc breakage and reformation characteristics weren't examined. The experiments in this chapter were designed to study this aspect further, and also to examine the impact of coagulation pH on NOM removal and floc properties. The experimental results were enhanced by measurements of zeta potential and turbidity which wasn't available during the previous jar tests. The reasoning for studying the effect of pH was two-fold:

1. On the full scale plant, the coagulation pH is controlled by lime dosing which frequently fails causing either an increase in pH or a decrease.
2. Coagulation mechanisms are known to be different at high pH (sweep flocculation) and low pH (patchwork agglomeration effects) – this may alter the floc strength and reformation properties.

The above shows that there was both a practical aspect to studying the effect of pH on floc properties and NOM removal, and also a research interest to investigate whether the impacts of coagulation pH on floc properties could be observed by the PDA and related to NOM removal. The same breakage jar test procedure was employed during these jar tests as for the previous jar tests carried out at UCL laboratories detailed in Chapter 3. The main differences between the sets of experiments was the use of the Aztec 2000 jar test equipment, and the use of Ferripol XL in place of the Sigma Aldrich ferric sulphate as specified in Chapter 3. Ferripol XL is the most common ferric based coagulant used in the water industry in the UK. A Malvern zetasizer 2000 was also used in these tests to measure the zeta potential before and after the tests.

Conventional jar tests were performed alongside the breakage jar tests, and the results were compared by the t-Test to assess if there was any effect attributable to the breakage test on parameters such as UV_{254} absorbance, turbidity and zeta potential. The significance testing results shown in table 16 showed that in the majority of cases there was no effect of the breakage test on the settled water quality measurements.

Settled Water Quality Parameter	Ferric:DOC Ratio	Coagulation pH	T-test probability factor (p)	Significant (Yes/No)
Turbidity	1.4	3.5	0.07	No
	1.4	4.5	0.42	No
	1.4	6.5	0.06	No
	1.7	3.5	0.20	No
	1.7	4.5	0.86	No
	1.7	6.5	0.11	No
	2	3.5	0.04	Yes
	2	4.5	0.01	Yes
	2	6.5	0.45	No
Zeta Potential	1.4	3.5	0.44	No
	1.4	4.5	0.01	Yes
	1.4	6.5	0.07	No
	1.7	3.5	0.92	No
	1.7	4.5	0.47	No
	1.7	6.5	0.49	No
	2	3.5	0.08	No
	2	4.5	0.70	No
	2	6.5	0.40	No
UV_{254} Absorbance	1.4	3.5	0.12	No
	1.4	4.5	0.44	No
	1.4	6.5	0.68	No
	1.7	3.5	0.49	No
	1.7	4.5	0.09	No
	1.7	6.5	0.48	No
	2	3.5	0.23	No
	2	4.5	0.57	No
	2	6.5	0.75	No

Table 16 t-Test p values at 95% significance level from comparisons between settled zeta potential, turbidity and UV_{254} absorbance measurements from jar tests and breakage jar tests.

The test types and measurements carried out at each dose and coagulation pH are summarised for clarity in table 17:

Test Type	Repeat Tests per experiment	UV_{254}	Zeta Potential	Turbidity	Dynamic Flocculation
Jar Test	4	Yes	Yes	Yes	No
Breakage Jar Test	4	Yes	Yes	Yes	Y

Table 17 Jar tests and breakage jar tests carried out during onsite testing at Albert WTW, March 2003

Part 5.0.0 Jar Tests to investigate the effect of Ferripol XL dose and coagulation pH on NOM removal and dynamic flocculation parameters

The coagulation pH on the full-scale plant was set to pH 4.2 - 4.5 which corresponded to the literature quoted optimum pH for ferric salts. It is easy to see that plant malfunction could lead to operation outside of this narrow range due to failures within the lime dosing plant. Operational knowledge suggests that the coagulation pH reduced to approximately pH 3.5 on occasions when the lime dosing failed due to blockages in the dosing line. There have also been occasions when the lime make-up strength has been changed and as a result the pH has increased to approximately 6.5. On the full-scale plant, good coagulation pH control is crucial to achieving a good final water quality and it is generally noted by plant operators that uncontrolled pH changes due to failure of lime dosing detrimentally effect the final water quality, implying that poorly coagulated particles break through the plant filters thereby increasing the risk of cryptosporidium breakthrough and inadequate disinfection. It is therefore important to understand more about the floc properties outside of the optimum coagulation pH.

The correct coagulant dose is also crucial to achieving efficient NOM removal within the process, and for this reason the effect of varying the ferric dose was considered. The impact of ferric dose relative to the DOC content has also been related to floc properties by Jarvis *et al.* (2005). In this set of experiments the Fe:DOC ratios applied were 1.4, 1.7 and 2. The range of doses of Ferripol XL used in this test were designed to study the conditions above the optimum dose as operational knowledge suggests that over-dosing is a common response to changes in raw water quality. The optimum Fe:DOC ratio for good NOM removal and floc strength as measured by the Mastersizer has previously been reported at around 1 (Jarvis *et al.*, 2005).

Part 5.0.1 Bulk Sample Raw Water Properties

The 70 litre bulk sample of raw water obtained at the start of the tests and used for all the jar tests and breakage jar tests and was analysed for UV_{254} absorbance, turbidity, zeta potential and pH prior to the start of each test. Table 18 shows the mean raw water quality parameters of raw water used for the jar tests. The number of samples was 18 (exception of DOC where only 1 sample obtained). The data suggests a good stability of the sample over the experimentation period and raw water quality was not considered to be a variable in these tests.

Parameter	UV_{254} Absorbance (abs/m)	Zeta Potential (mV)	Turbidity (NTU)	pH	DOC (mg/l)	SUVA (m -1 L/mg C)
Value	34	-15	7	6.16	6.9	4.9
Standard Error	0.3	0.3	0.3	0.05	*	

Table 18 Mean raw water bulk sample parameters during onsite jar tests at Albert WTW, March 2003. * 1 sample taken.

The laboratory temperature remained at a constant 15ºC throughout the duration of the jar tests and the sample was left to acclimatise before starting the jar tests. The raw water temperature at source (bank-side storage Albert WTW reservoir) was 8ºC.

Part 5.1 Jar test and breakage jar test settled water quality results and discussion

Table 19 shows the mean water quality parameters measured during the experiments using Ferripol XL at the three coagulation pH conditions. .

	Fe:DOC Ratio	Coagulation pH	Raw UV_{254} (abs/m)	Residual UV_{254} (abs/m)	UV_{254} Removal (%)	Raw Zeta Potential (mV)	Settled Zeta Potential (mV)	Raw Turbidity (NTU)	Settled Turbidity (NTU)
Jar Tests	1.4	3.5	35	14.2 (0.2)	58	-15.8	5.0 (0.2)	5.8	5.8 (0.3)
	1.7	3.5	34	14.9 (0.3)	56	-17	5.6 (0.3)	5.5	9.2 (0.5)
	2	3.5	34	15.2 (0.1)	55	-15.1	5.1 (0.1)	3.7	9.1 (0.5)
	1.4	4.5	35	4.3 (0.1)	87	-15.5	-0.4 (0)	6.9	2.2 (0.6)
	1.7	4.5	33	3.0 (0.1)	91	-16.3	2.9 (0.2)	7.9	3.2 (0.9)
	2	4.5	34	3.9 (0.1)	88	-14.85	3.7 (0.1)	7.5	2.7 (0.4)
	1.4	6.5	34	4.1 (0)	88	-14	-11.1 (0.9)	7.4	1.8 (0.3)
	1.7	6.5	34	5.6 (0.1)	83	-14.8	-10.6 (0.6)	6.8	3.3 (0.5)
	2	6.5	30	2.7 (0.1)	92	-13.1	-0.7 (0.8)	6.1	2.4 (0.7)
Breakage Jar Tests	1.4	3.5	35	13.6 (0.2)	60	-15.8	5.0 (0.2)	5.1	5.1 (0.4)
	1.7	3.5	34	14.5 (0.2)	57	-16.7	5.6 (0.3)	5.5	8.1 (0.3)
	2	3.5	34	14.9 (0.3)	56	-15.1	4.7 (0.2)	7.5	6.8 (0.3)
	1.4	4.5	35	3.8 (0.1)	89	-15.5	1.7 (0.3)	6.9	2.6 (0.3)
	1.7	4.5	33	1.8 (0.1)	95	-16.3	2.5 (0.2)	7.9	3.1 (0.5)
	2	4.5	34	4.1 (0.1)	88	-14.85	3.8 (0.2)	7.5	4.9 (0.2)
	1.4	6.5	34	5.0 (0.1)	85	-14	-14.6 (0.4)	7.4	2.1 (0.3)
	1.7	6.5	34	6.6 (0)	80	-14.8	-10.0 (1.1)	6.8	2.3 (0.3)
	2	6.5	30	2.9 (0.2)	91	-13.1	-0.1 (0.6)	6.1	3.0 (0.5)

Table 19 Mean water quality data from jar tests and breakage jar tests using Ferripol XL onsite at Albert WTW, March 2003, SE in parentheses

It was noted throughout the experiments that there appeared to be a subtle difference between the water quality data obtained from the jar tests and the breakage tests. This has been looked at in closer detail to determine whether the results from both sets of tests can be combined to look at overall trends. The t-Test probabilities show that there was only three cases of significant difference between the two data-sets and that was the settled zeta potential at coagulation pH 4.5 and 10 mg/l Ferripol XL as Fe^{3}, and settled turbidity at pH 3.5 and 4.5 at 14 mg/l Ferripol XL as Fe^{3} . Overall the difference was not found to be significant and the data from both sets of jar tests were combined for the results analysis.

Part 5.1.0 Sensitivity of jar test parameters to Ferripol XL dose changes

Table 20 shows the T-test probability factors for each coagulation pH considering the effect of incremental Ferripol XL dose. This shows that turbidity was the least affected by the changes in coagulant dose, with 6 out of 9 systems showing no significant difference between the doses. Zeta potential showed the greatest sensitivity to dose change with only 1 test out of 9 showing no significant difference at pH 3.5 between 10 mg/l Ferripol XL as Fe^{3+} and 14 mg/l F Ferripol XL as Fe^{3+}. At coagulation pH 4.5 there was no significant difference between the three Ferripol XL doses with respect to UV_{254} absorbance. Overall zeta potential and UV_{254} absorbance were the most sensitive parameters with respect to change in coagulant dose at a specified pH. Zeta potential was the most sensitive parameter to changes in Ferripol XL dose. The same exercise was repeated for sensitivity to coagulation pH and results shown in table 21. The effect of Ferripol XL dose and pH, on dynamic flocculation properties wasn't analysed using the T-test, as there were only 3 repeat tests carried out rather than 8 and the result would not be considered a strong result.

Settled Water Quality Parameter	Coagulation pH	Ferric:DOC Ratio	T-test probability factor (p)	Significant (Yes/No)
Turbidity	3.5	1.4 and 1.7	0.00	Yes
		1.4 and 2	0.00	Yes
		1.7 and 2	0.23	No
	4.5	1.4 and 1.7	0.17	No
		1.4 and 2	0.03	Yes
		1.7 and 2	0.37	No
	6.5	1.4 and 1.7	0.06	No
		1.4 and 2	0.05	No
		1.7 and 2	0.93	No
Zeta Potential	3.5	1.4 and 1.7	0.02	Yes
		1.4 and 2	0.15	No
		1.7 and 2	0.01	Yes
	4.5	1.4 and 1.7	0.00	Yes
		1.4 and 2	0.00	Yes
		1.7 and 2	0.00	Yes
	6.5	1.4 and 1.7	0.03	Yes
		1.4 and 2	0.00	Yes
		1.7 and 2	0.00	Yes
UV_{254} Absorbance	3.5	1.4 and 1.7	0.00	Yes
		1.4 and 2	0.00	Yes
		1.7 and 2	0.16	No
	4.5	1.4 and 1.7	0.05	No
		1.4 and 2	0.76	No
		1.7 and 2	0.18	No
	6.5	1.4 and 1.7	0.01	Yes
		1.4 and 2	0.02	Yes
		1.7 and 2	0.00	Yes

Table 20 t-Test p values at 95% significance level from comparisons of settled zeta potential, turbidity and UV_{254} absorbance using Ferric:DOC ratio 1.4, 1.7 and 2 at coagulation pH 3.5,4.5 and 6.5.

Part 5.1.1 Sensitivity of jar test parameters to coagulation pH changes

Table 21 shows that in general most of the measured parameters were sensitive to pH changes. Settled turbidity showed no difference between pH 4.5 and pH 6.5 at all three Ferripol XL doses. Zeta potential and UV_{254} absorbance showed heightened sensitivity to pH changes with the exception of the tests carried out at pH 4.5, and pH 6.5 using 10 mg/l Ferripol XL as Fe^{3+}.

The change in coagulation pH could therefore be said to be more significant than changes in Ferripol XL dose in terms of the effect on the treated water quality.

Settled Water Quality Parameter	Ferric:DOC Ratio	Coagulation pH	T-test probability factor (p)	Significant (Yes/No)
Turbidity	1.4	3.5 and 4.5	0.03	Yes
		3.5 and 6.5	0.01	Yes
		4.5 and 6.5	0.22	No
	1.7	3.5 and 4.5	0.00	Yes
		3.5 and 6.5	0.00	Yes
		4.5 and 6.5	0.59	No
	2	3.5 and 4.5	0.00	Yes
		3.5 and 6.5	0.00	Yes
		4.5 and 6.5	0.07	No
Zeta Potential	1.4	3.5 and 4.5	0.02	Yes
		3.5 and 6.5	0.01	Yes
		4.5 and 6.5	0.01	Yes
	1.7	3.5 and 4.5	0.01	Yes
		3.5 and 6.5	0.01	Yes
		4.5 and 6.5	0.03	Yes
	2	3.5 and 4.5	0.02	Yes
		3.5 and 6.5	0.01	Yes
		4.5 and 6.5	0.01	Yes
UV_{254} Absorbance	1.4	3.5 and 4.5	0.01	Yes
		3.5 and 6.5	0.00	Yes
		4.5 and 6.5	0.94	No
	1.7	3.5 and 4.5	0.00	Yes
		3.5 and 6.5	0.01	Yes
		4.5 and 6.5	0.01	Yes
	2	3.5 and 4.5	0.02	Yes
		3.5 and 6.5	0.01	Yes
		4.5 and 6.5	0.02	Yes

Table 21 t-Test p values at 95% significance level from comparisons of settled zeta potential, turbidity and UV_{254} absorbance at coagulation pH 3.5,4.5 and 6.5 using Ferric:DOC ratio 1.4,1.7 and 2.

Part 5.2 The effect of coagulation pH on NOM removal

The effect of coagulation pH on the mean residual UV_{254} absorbance is shown in figure 50. The lowest residual of 2.7 abs/m was recorded at pH 6.5 using 14 mg/l Ferripol XL as Fe^{3+} and the highest residual level of 16.4 abs/m at pH 3.5, and 12 mg/l Ferripol XL as Fe^{3+}. The removal at coagulation pH 4.5 was high for all Ferripol XL doses, but not as high as the removal seen in chapter 5 results at Fe:DOC ratio of 1.3. The increased removal observed using 14 mg/l at pH 6.5 is not significant enough to justify the chemical cost, and would be highly likely to over-load downstream solid removal processes. It has to be concluded that a coagulation pH of 4.5 was a more operable system. The UV_{254} absorbance removal measured at pH 3.5 would present an unacceptable risk of forming THM's during disinfection with chlorine. The tests confirmed that coagulation pH is a very important factor that has a marked detrimental effect at low pH. It was surprising that the performance at coagulation pH 4.5 was not sensitive to Ferripol XL dose, as the performance in the previous set of jar tests in Chapter 4 showed a deterioration at around 1.7 Fe:DOC.

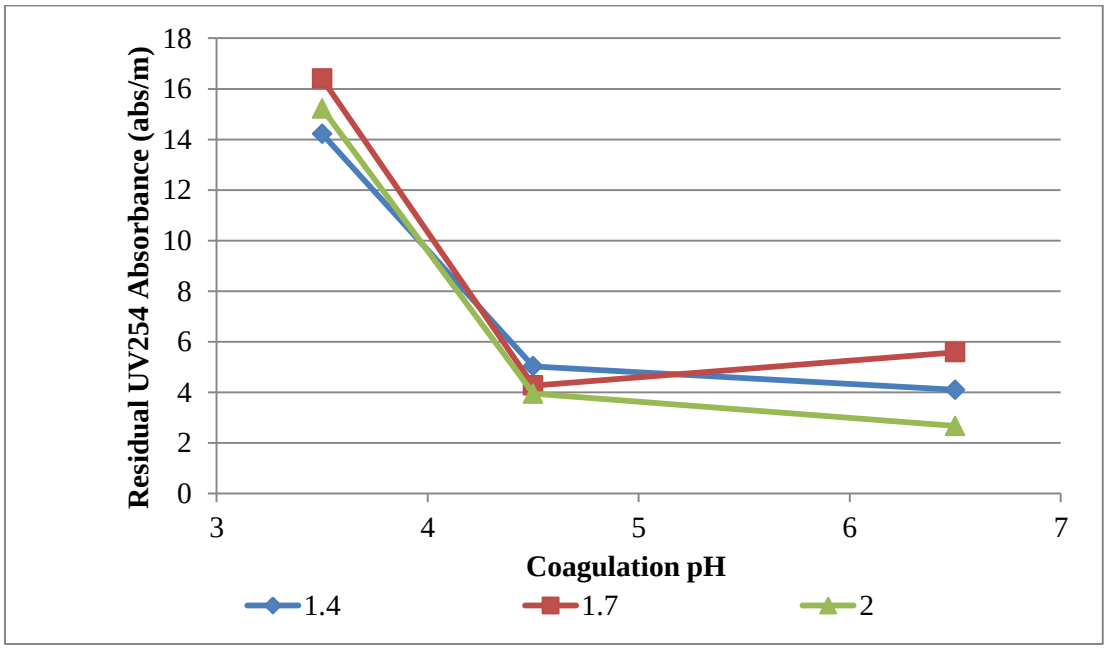


Figure 50 Relationship between residual UV_{254} absorbance and coagulation pH using Ferripol XL at Ferric:DOC ratios of 1.4,1.7 and 2 during jar tests at Albert WTW March 2003,Raw water UV_{254} absorbance 34 abs/m

Part 5.3 The effect of coagulation pH and Ferripol XL dose on settled zeta potential

Figure 51 shows that at coagulation pH 3.5, the zeta potential remained constant, positive and independent of changes in coagulant dose. At coagulation pH 4.5 and a dose of 10 mg/l Ferripol XL as Fe^{3+} the zeta potential was close to zero, and increased with increasing coagulant dose. As the pH increased from 3.5 to 6.5, the zeta potential decreased as would be expected, for all doses of Ferripol XL. At pH 3.5 it is likely that the NOM was more positively charged and repellent to the coagulant therefore explaining the poor removal observed. The functional groups, such as the carboxylic acid groups are likely to be less ionised at lower pH values, and therefore less able to interact with the positively charged coagulant.

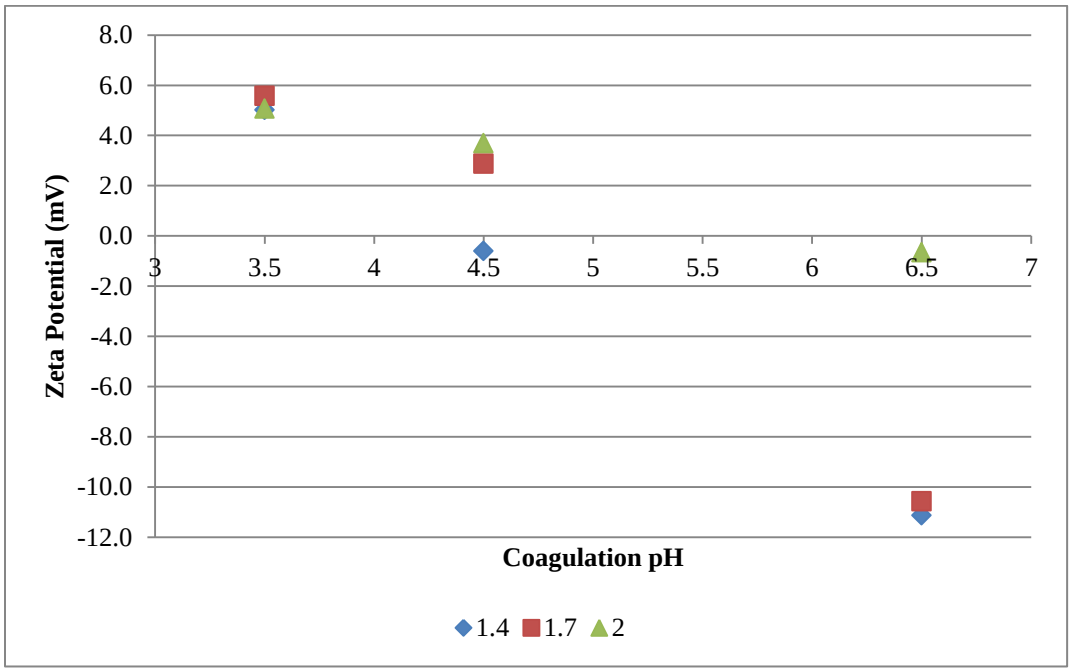


Figure 51 Relationship between zeta potential and coagulation pH using Ferripol XL at Ferric:DOC ratios of 1.4,1.7 and 2 during jar tests at Albert WTW March 2003, Raw water zeta potential -15 mV

Considering the direct relationship between coagulation pH and zeta potential, it is logical to look at the relationship between zeta potential and UV_{254} absorbance removal next.
Figure 52 shows the correlation between zeta potential and residual UV_{254} absorbance obtained from the dosing trial results – from both sets of jar tests. A clear cut-off is seen at zeta potential values above +4 mV, with a considerable marked increase in residual UV_{254} absorbance above

this value. This data suggests that the upper limit of zeta potential should be +4 mV for this raw water and the conditions applied. The lower limit is less obvious as good performance was obtained at -11 mV for one set of tests (using 10mg/l Ferripol XL as Fe^{3+} as pH 6.5), but not at -10.5 mV or for -9.95 mV. Zeta potential is often used as a performance parameter, with the proviso being that the operational window has to be determined by experience for the given system. Work with the same raw water source showed that a zeta potential range of –10mV to +3 mV was representative of a safe operational window based on NOM removal as measured by DOC. Based on the aforementioned operational window, and the results shown in figure 52 the majority of the jar test systems were just outside of the operational window of -10 mV to +4 mV, with the exceptions being pH 4.5 10 mg/l, pH 4.5 12 mg/l and pH 6.5 14 mg/l. The difference could be down to differences in the method of analysing the humic substances, DOC measurement being a more compound specific analysis than UV_{254} absorbance.

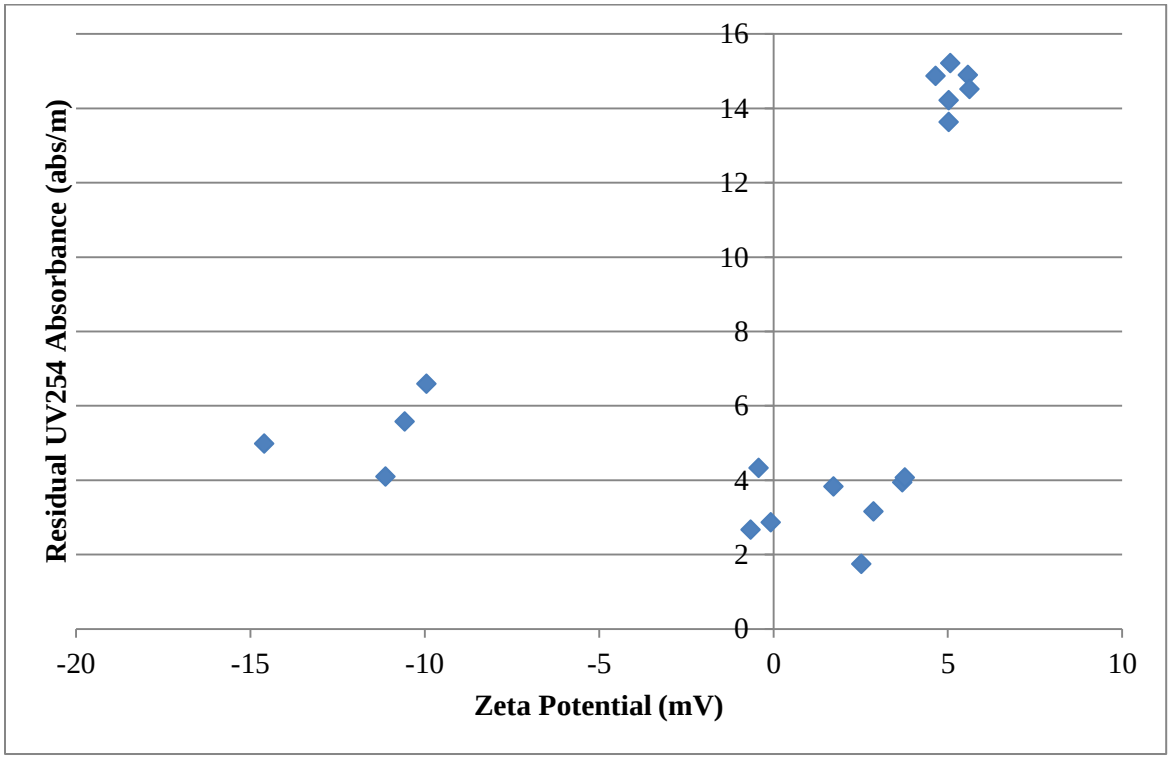


Figure 52 Relationship between zeta potential and residual UV_{254} absorbance using Ferripol XL at Ferric:DOC ratios of 1.4,1.7 and 2 during jar tests at Albert WTW March 2003, Raw water UV_{254} absorbance 34 abs/m

Part 5.4 The effect of zeta potential on settled turbidity

Figure 53 shows a clear increase in turbidity with increasing zeta potential above 4 mV. This further corroborates the existence of an operational window, outside of which the performance is sub-optimal. The lower end of the operational window is still difficult to pin-point, as the performance is similar to that of the mid-range, but the upper end is clearly seen by a step-change in turbidity from approximately 3 NTU to 5 NTU which was a significant change at the 95% confidence level (p =0.001).

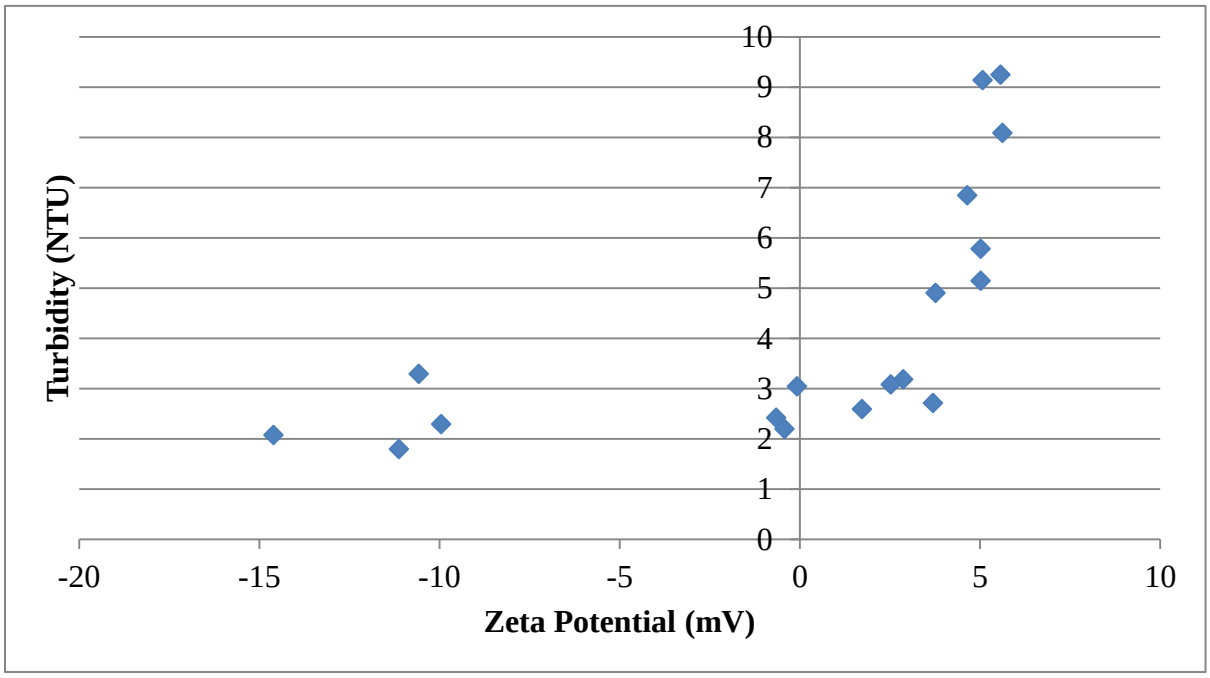


Figure 53 Relationship between zeta potential and settled turbidity using Ferripol XL at Ferric:DOC ratios of 1.4,1.7 and 2 during jar tests at Albert WTW March 2003, raw water turbidity 8 NTU

Part 5.5 Dynamic flocculation data from breakage tests using Ferripol XL at coagulation pH 3.5, 4.5 and 6.5

Figure 54 shows the dynamic flocculation curves illustrating the floc growth, breakage and reformation stages of the breakage jar test for each coagulation pH condition and Ferripol XL dose. At coagulation pH 3.5 and 14 mg/l Ferripol XL as Fe^{3+} which has already been established as a poor condition for NOM removal, the floc formation and reformation was far greater than the rest of the systems

This result is counter-intuitive as poorly charge-neutralised NOM would not be expected to coagulate well enough to form reversible floc, and especially not more reversible than well charge-neutralised floc. This points to charge neutralisation of a specific fraction of NOM which is reactive at pH 3.5, and able to form more stable aggregates. The ratio of Fe/DOC was still important at pH 3.5 with respect to floc size but not UV_{254} absorbance removal within the range of doses applied.

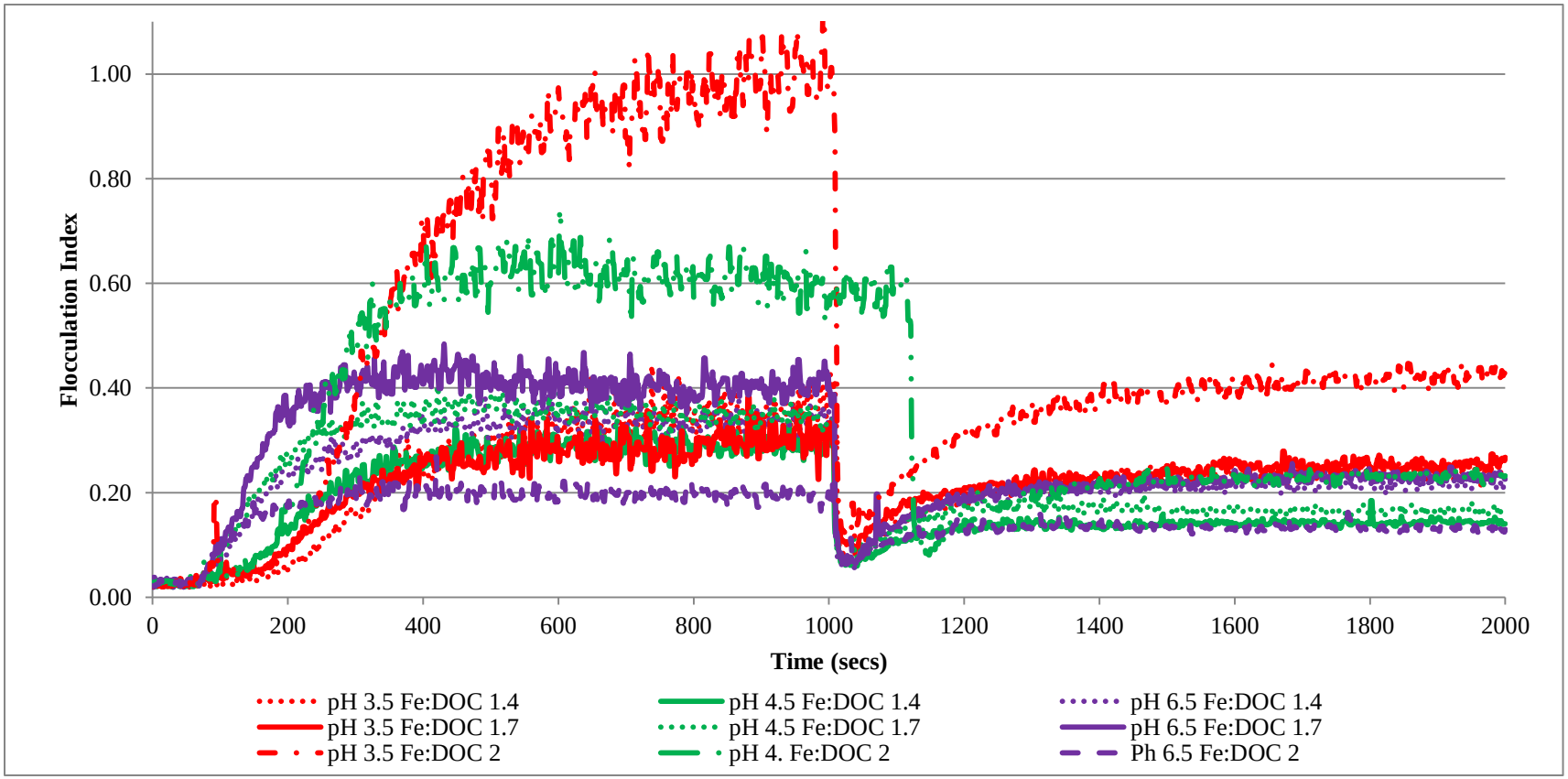


Figure 54 Dynamic flocculation curves from breakage jar tests at Albert WTW using Ferripol XL at coagulation pH 3.5, 4.5 and 6.5 and at Ferric:DOC ratios of 1.4,1.7 and 2, March 2003

The standard error between each of the 3 flocculation curves was very low implying good reproducibility between the three controlled tests. This means that there is a good degree of confidence in the computed values of the floc reformation factor and the floc strength factor. Table 22 shows the mean dynamic flocculation parameters using Ferripol XL at coagulation pH 3.5, 4.5 and 6.5.

Coagulation pH	Ferripol XL Dose as Fe3+ (mg/l)	Fe:DOC Ratio	R_{FI}	FI_{max}	FI_{break}	FI_{ref}	Floc Strength Factor	Floc Reformation Factor
3.5	10	1.4	0.0009	0.3 (0.01)	0.07 (0.02)	0.24 (0.01)	0.23	0.74
3.5	12	1.7	0.0015	0.38 (0.001)	0.09 (0.03)	0.24 (0.01)	0.24	0.52
3.5	14	2	0.003	1 (0.02)	0.01 (0.02)	0.43 (0.02)	0.11	0.36
4.5	10	1.4	0.0011	0.34 (0.01)	0.06 (0.03)	0.14 (0.01)	0.18	0.29
4.5	12	1.7	0.0019	0.4 (0.002)	0.07 (0.01)	0.16 (0.01)	0.18	0.27
4.5	14	2	0.0036	0.6 (0.01)	0.11 (0.06)	0.21 (0.01)	0.18	0.20
*6.5	10	1.4	0.0014	0.4 (0.01)	0.06 (0.03)	0.22 (0.01)	0.15	0.47
*6.5	12	1.7	0.0033	0.34 (0.01)	0.06 (0.02)	0.23 (0.01)	0.18	0.61
*6.5	14	2	0.0020	0.2 (0.01)	0.07 (0.01)	0.13 (0.01)	0.35	0.46

Table 22 Mean dynamic flocculation parameters using Ferripol XL at different coagulation pH, onsite tests at Albert WTW March 2003

***Dynamic flocculation parameters subject to error due to Yu *et al.* (2010)**

Part 5.6 The effect of coagulation pH and coagulant dose on dynamic flocculation performance parameters

Figure 55 shows that at all pH conditions there was little difference in maximum flocculation index as the Ferripol XL dose increased from 10 mg/l as Fe^{3+} to 12 mg/l as Fe^{3}. As the dose was increased to 14 mg/l as Fe^{3+}, there was a marked difference in floc size between the three pH conditions with the largest being formed at pH 3.5 and the smallest at pH 6.5. The result at pH 6.5 may not be entirely representative as it is highly likely that the mode of coagulation at pH 6.5 is that of sweep flocculation as mentioned earlier. It has been noted by Yu *et al*. (2010) that the PDA floc index results (and other similar light scattering techniques) in the sweep flocculation mode are subject to error as the floc size as measured by the floc index may not be proportionate to the actual floc size due to the mechanism of formation of the primary particles. The particulate formed during "sweep" flocculation is primarily hydroxide sols that have adsorbed NOM attached, these particles are thought to have a low refractive index, and can have extinction cross sections much less than their projected area. These flocs may therefore appear much smaller than they actually are. The results at 1.4 and 1.7 appeared to be consistent with visual appearance but it was difficult to be exact. This effect has been noted with alum/kaolin systems and alum/humic systems and it is logical to assume that the same would be true of ferric/humic systems.

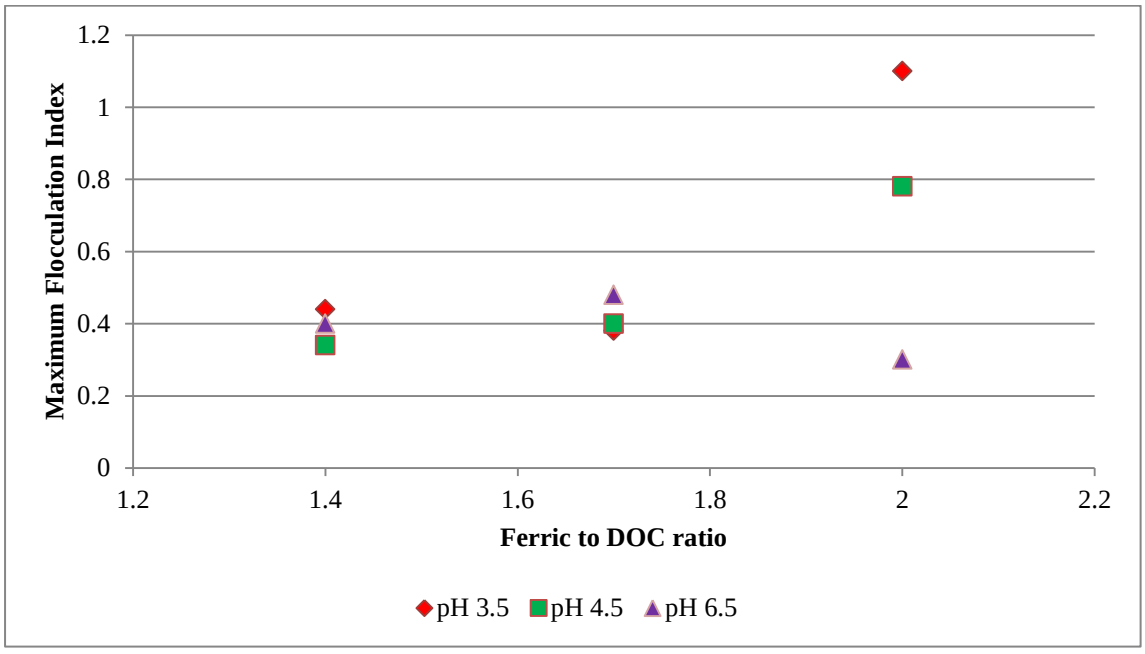


Figure 55 Correlation between $FI_{max,}$ coagulation pH and Ferripol XL dose relative to DOC, Onsite jar tests Albert WTW March 2003

Figure 56 shows the correlation between zeta potential, residual UV_{254} absorbance and floc reformation factor. This shows that as the settled zeta potential increased beyond 3 mV, the reformation factor increased sharply. The trend prior to that appeared to show that the reformation factor decreased with increasing zeta potential, but it is difficult to tell exactly as there were no zeta potential values generated in the range of -10 mV to 0 mV. The result beyond 3 mV is interesting as it contradicts the performance observed with respect to turbidity and residual UV_{254} absorbance, which showed a marked deterioration. This result is counter-intuitive as it would be expected that floc reformation would deteriorate when conditions for complete charge-neutralisation were sub-optimal as is clearly the case at zeta potential values above +4 mV. The results suggest that reversible floc formation may not be positively related to humic substance removal.

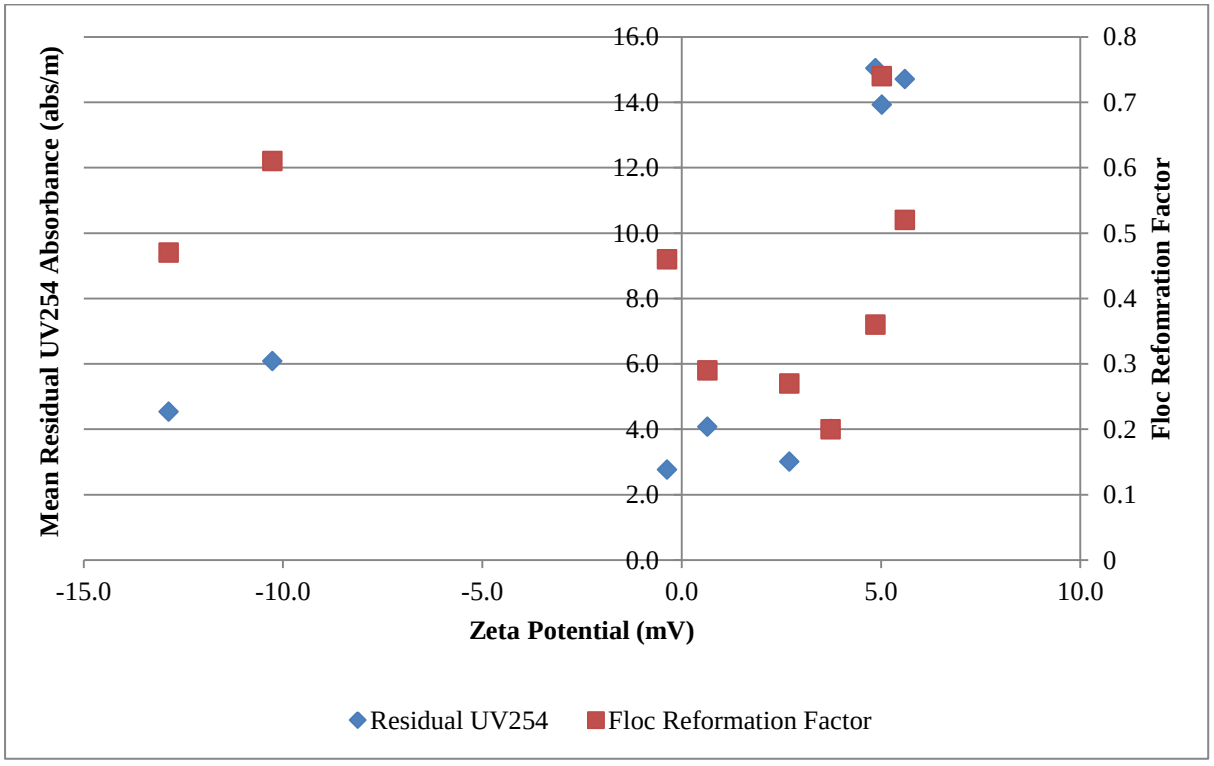


Figure 56 Relationship between floc reformation factor, residual UV_{254} absorbance and zeta potential at using Ferripol XL at coagulation pH 3.5, 4.5 and 6.5 and at Ferric:DOC ratios of 1.4,1.7 and 2, March 2003

Figure 57 shows that there is no clear relationship between floc strength factor and residual UV_{254} absorbance, or zeta potential. This indicates that floc strength factor was independent of zeta potential, and NOM removal performance.

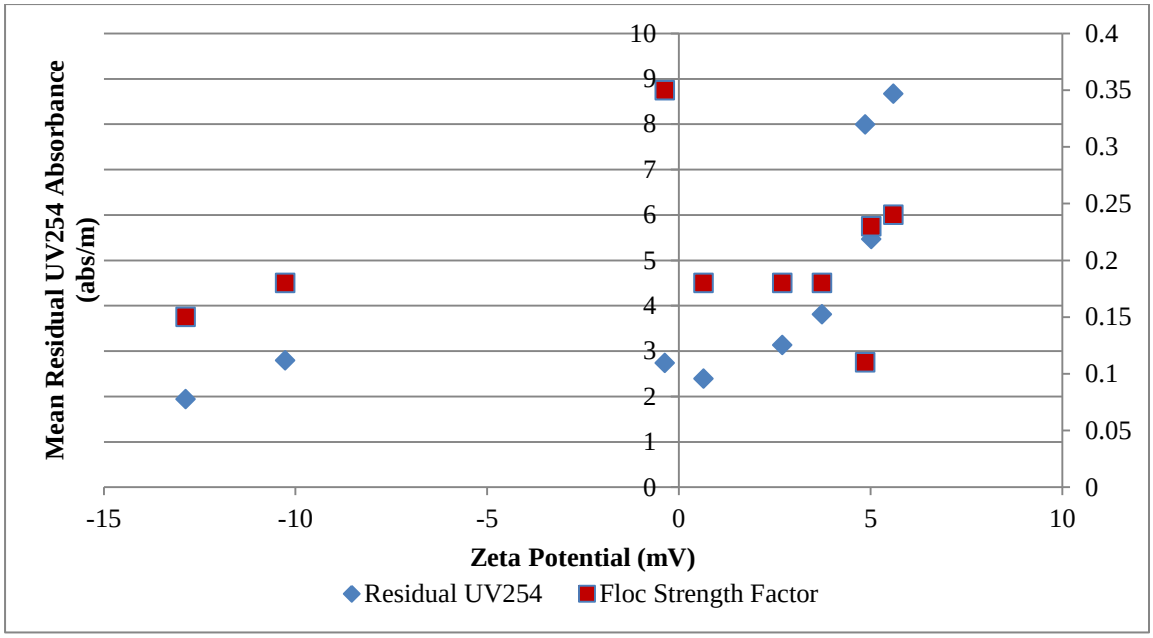


Figure 57 Relationship between floc strength factor, residual UV_{254} absorbance and zeta potential using Ferripol XL at coagulation pH 3.5, 4.5 and 6.5 and at Ferric:DOC ratios of 1.4,1.7 and 2, March 2003

Figure 58 shows that there was a tendency towards a decrease in floc strength factor as floc size increased. The general trend between floc size and strength factor shown in figure 58 was also observed using ferric sulphate and polymeric additives which was presented in Chapter 4.

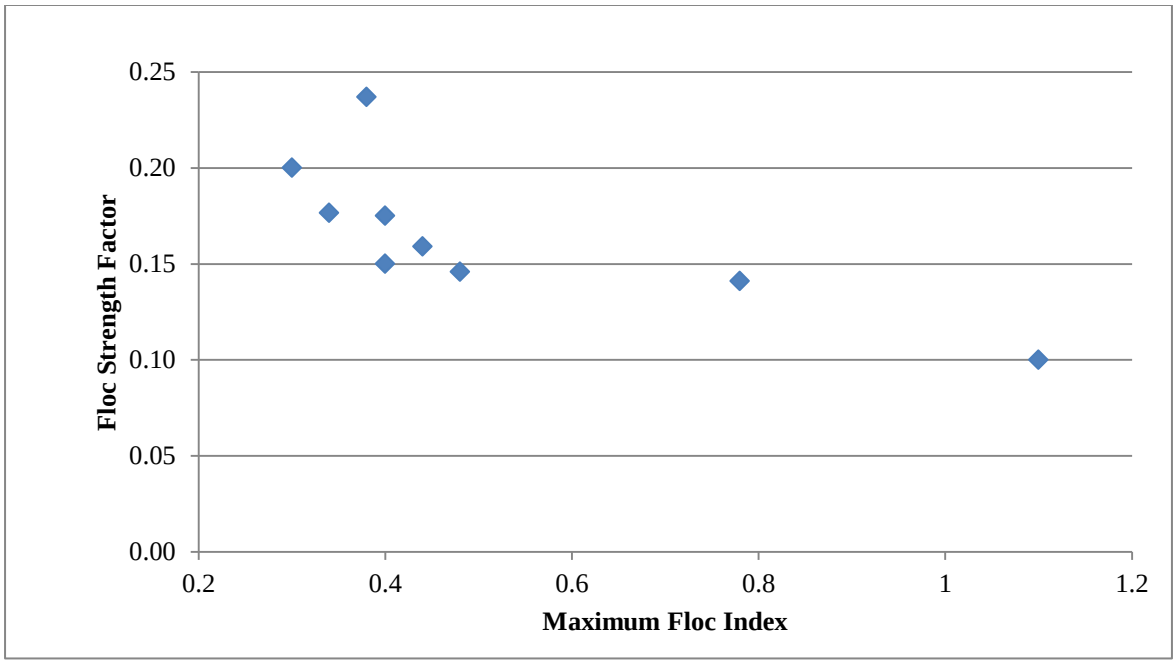


Figure 58 Relationship between floc strength factor and maximum floc index using Ferripol XL at coagulation pH 3.5, 4.5 and 6.5 and at Ferric:DOC ratios of 1.4,1.7 and 2, March 2003

Figure 59 shows that the maximum rate of increase in flocculation index is strongly related to Ferripol XL dose with the fastest rates observed at the highest doses under each pH condition, and the slowest rates at 1.4 Fe:DOC. The NOM removal was considerably worse at pH 3.5, so it is surprising that the flocculation rate was very similar at pH 3.5 compared to pH 4.5 and 6.5 at the same dose ratio of 1.4 Fe:DOC . The magnitude of difference was more marked at the higher Ferripol doses. This suggests that the maximum flocculation rate is heavily influenced by the concentration of coagulant, and by the pH conditions. At coagulation pH 4.5, the sensitivity analysis showed that the residual UV_{254} absorbance was not affected by the Ferripol XL dose in a significant way. Figure 59 shows a three-fold increase in maximum flocculation rate as the Fe:DOC ratio was increased from 1.4 to 2. This suggests that this parameter may not be particularly useful when optimising dose within a narrow range.

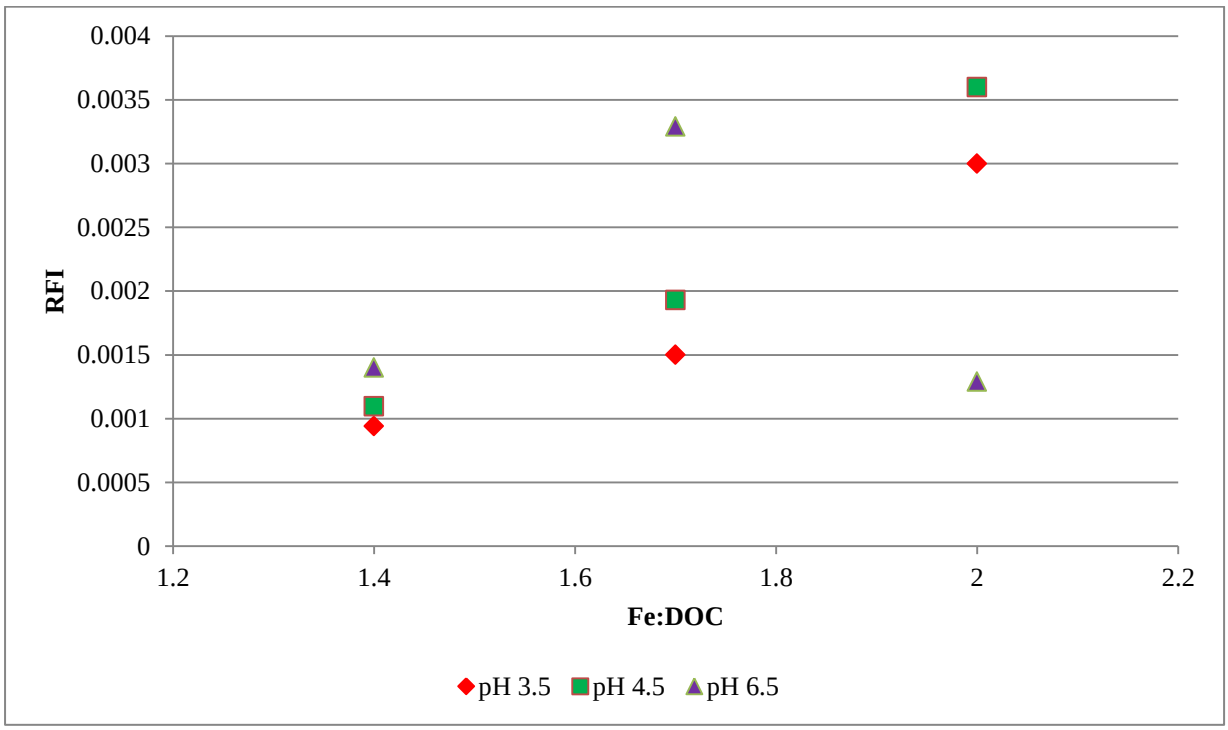


Figure 59 Correlation between R_{FI} and Ferripol XL dose relative to DOC content at pH 3.5,4.5 and 6.5, Onsite jar tests at Albert WTW March 2003

Figure 60 shows the early part of the flocculation curves for all systems studied. This shows that time taken for flocculation rate to enter the exponential phase varied considerably between the systems with the slowest systems observed at pH 3.5, and the fastest systems at pH 6.5 and pH 4.5.

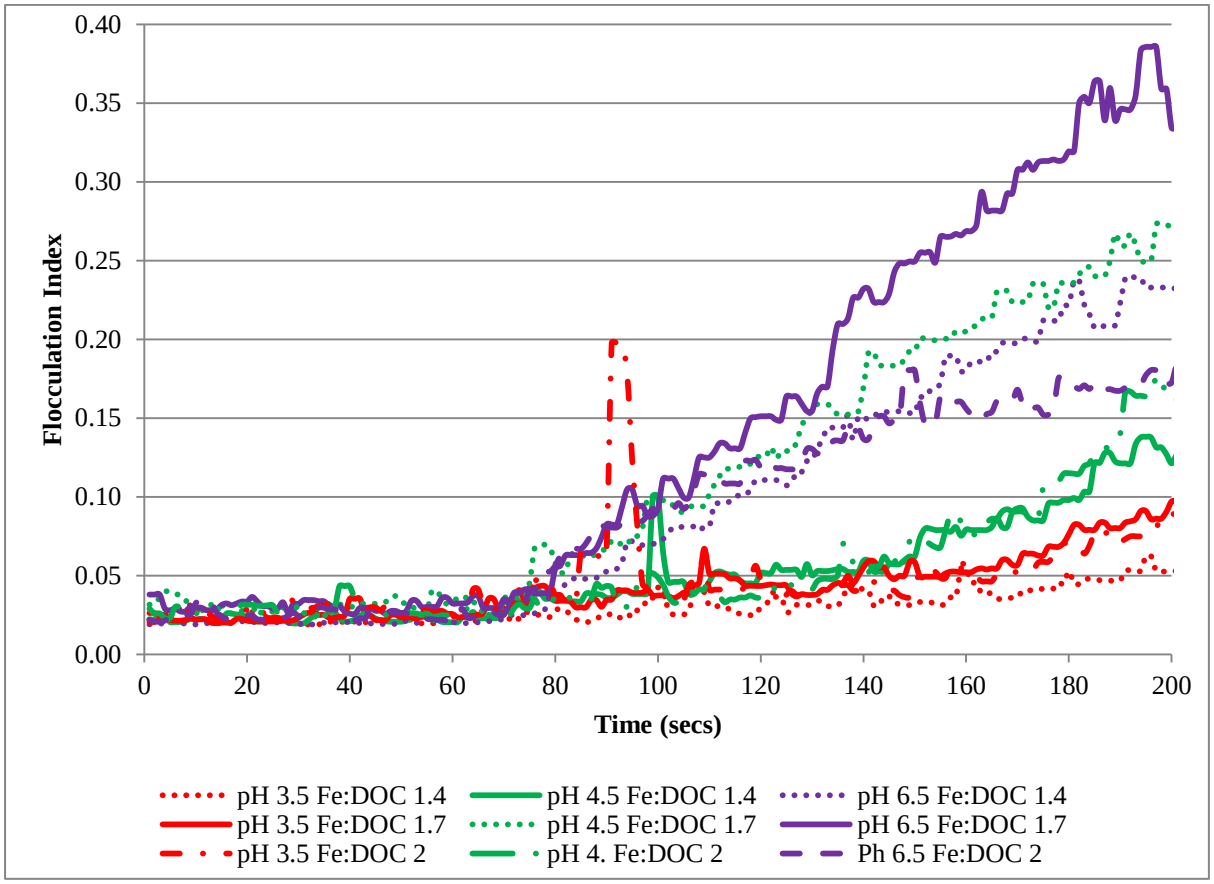


Figure 60 Initial Flocculation Curves using Ferripol XL using Ferripol XL at coagulation pH 3.5, 4.5 and 6.5 and at Ferric:DOC ratios of 1.4,1.7 and 2, March 2003

Part 5.7 Results summary and discussion

Jar tests were carried out as well as breakage jar tests in these experiments. Comparison of the settled zeta potential, residual UV_{254} absorbance and turbidity between the jar tests and the breakage jar tests at 95% significance level showed that there was no significant difference. This eliminated the effect of the breakage period on the water quality parameters mentioned above. There were two controlled parameters investigated during these experiments:

- Coagulation pH.
- Fe:DOC ratio within an over-dose range.

It is useful to summarise the main findings from these experiments in relation to the effects of changes made to the two controlled parameters of pH and dose on the water quality parameters, and dynamic flocculation parameters.

Part 5.7.0 Effect of coagulation pH and Fe:DOC ratio on NOM removal performance

The findings from all three sets of jar tests showed that NOM removal as measured by UV_{254} absorbance was very similar and good at pH 4.5 and pH 6.5, but poor at pH 3.5. The Fe:DOC ratio studied at each coagulation pH condition was 1.2, 1.7 and 2.0. At coagulation pH 3.5 the impact of increased Fe:DOC ratio on the residual UV_{254} absorbance was very slight. The fact that flocculation was observed at coagulation pH 3.5 and that there was some NOM removal (>50%) indicates that some fraction of the humic substance was reactive under acidic conditions. At pH 4.5 there was no impact of Fe:DOC on NOM removal which implies that there is no benefit to additional coagulant in this regard. At pH 6.5 the effect of dose was found to impact the residual NOM significantly, with a gradual reduction noted as the dose ratio increased to 2 which corresponded with a zeta potential of 0 mV. This system resulted in the best residual NOM but the reasons are unclear.

Overall the results showed that within the range of Fe:DOC used the optimum coagulation pH for NOM removal was mostly pH 4.5 which is consistent with the literature. It is acknowledged that the range of Fe:DOC applied was representative of over-dose conditions and better removals may have been achieved with a lower range closer to 1. Coagulation pH 6.5 performed well within the range of Fe:DOC applied but is not thought to be a viable pH to operate a full-scale plant as the quantities of sludge to process would be significantly higher as would the chemical costs.

Part 5.7.1 Effect of coagulation pH on floc properties

The impact of increasing the Fe/DOC ratio on the floc size as measured by FI_{max} was negligible (p value >0.05 indicating insignificant) between 1.2 and 1.7 at coagulation pH 3.5 and 4.5 but increased considerably as the Fe:DOC increased to 2.0. The visual results generated from the tests at pH 6.5 also indicated that there was an increase in floc size – the PDA results generated from pH 6.5 were not thought to be representative in terms of floc size. It has been noted by Yu *et al*. (2010) that the PDA floc index results (and other similar light scattering techniques) in the sweep flocculation mode are subject to error as the floc size as measured by the floc index may not be proportionate to the actual floc size due to the mechanism of formation of the primary particles.

The particulate formed during "sweep" flocculation is primarily hydroxide sols that have adsorbed NOM attached. These particles are thought to have a low refractive index, and can have extinction cross sections much less than their projected area; and therefore appear much smaller than they actually are. The mode of NOM removal is believed to be dominated by precipitation of metal hydroxides at pH >6 (Gregor *et al*., 1997). This implies that the mode of coagulation at pH 6.5 should have been that of "sweep flocculation" but the data showed that at pH 6.5 the zeta potential tended towards 0 mV as the Fe:DOC ratio increased. The zeta potential trend suggested charge neutralization as the mode of coagulation, rather than "sweep flocculation" but the PDA data did not agree with visual observations at Fe:DOC of 2.0.

The flocculation rate at Fe:DOC ratio of 2.0 was observed to tail off in comparison to the 1.2 and 1.7 thereby supporting a different mechanism for coagulation at this dose – formation of the hydroxide sols is reputed to be rapid and therefore "sweep flocculation" systems should flocculate faster than "charge neutralization" systems. The flocculation rate using Fe:DOC ratio of 2.0 would have been expected to be quicker than the Fe:DOC systems of 1.2 and 1.7 if "sweep flocculation" was the mode of operation. The zeta potential data actually suggests that "sweep flocculation" occurred at Fe:DOC ratio of 1.2 and 1.7 but "charge neutralization" was the more likely mechanism at Fe:DOC ratio of 2.0. It is also worth noting that the degree of UV_{254} absorbance removal was highest at this condition. If the zeta potential and UV_{254} absorbance removal data using Fe:DOC ratio of 2.0 were reviewed in isolation from the PDA data, then the results would suggest charge neutralization as the mechanism. In this case, the PDA data indicated that the mechanism was sweep flocculation. There may be a case to support the two processes occurring concurrently at this pH. There is a lack of literature studying these parameters on raw waters outside of the optimum coagulation pH of 4.5 and so it is difficult to validate against previous results. More study in this area would verify whether this is a repeatable result, although ultimately a coagulation pH of 6.5 would be costly and would most likely increase the solids loading on the downstream processes. The flocculation rate was measured in the previous set of experiments in Chapter 4 and the correlation between flocculation rate and UV_{254} absorbance removal was also noted to be positive. In this set of experiments the flocculation rate was heavily influenced by coagulant dose at each pH condition but the dose was independent of UV_{254} absorbance removal.

At the lower Fe:DOC ratios the difference in flocculation rate at each pH condition was minimal but as the Fe:DOC ratio increased the difference became more marked and the rate increased. This effect has also been observed by Jarvis *et al*., (2004) who noted that increased Fe:DOC had a dominating impact on the flocculation rate, and also floc size.

The range of coagulant doses used in this set of experiments compared to the previous set was smaller and most likely over-dose conditions – therefore the flocculation rate was not such a system-defining parameter as was the case in the first set of tests when the coagulant dose range was larger. This is an important factor to include when designing coagulant dose optimization strategy so that effort can be focused on the most influential parameters.
The effect of increasing Fe:DOC on floc size as measured by FI_{max} was also noted to be similar to the findings of Jarvis *et al*. (2004) who used a Mastersizer 2000. As the dose increased relative to the NOM concentration, the steric and repulsive effects of the NOM were reduced thereby enabling faster floc growth and larger flocs. The data presented in figure 55 suggested that there was a threshold Fe:DOC ratio independent of the pH condition between 1.7 and 2.0 whereby the floc size was influenced by the increased coagulant dose. There was little change in FI_{max} between Fe:DOC of 1.4 and 1.7, although the flocculation rate was influenced strongly throughout the range of Fe:DOC. A greater range of Fe:DOC would have been beneficial in identifying the threshold for increase in FI_{max}. In this work the findings of Duan and Gregory (2002) and Jarvis *et al*. (2004) at optimum pH 4.5, with respect to the relatively smaller size of "charge neutralization" flocs compared to bridging and sweep flocs was confirmed as true.

Part 5.7.2 Zeta potential and pH/Ferripol XL dose

Work by Sharp *et al.* (2006) on the same raw water source provided evidence for an operational window for zeta potential, within which NOM removal is optimal. This window was documented to be -10mV to +3 mV. These results also confirm the operational window and provide some evidence to extend the upper bound to +4 mV. Fe:DOC ratio has already been shown to have had an impact on flocculation rate, and FI_{max} but there was no appreciable impact on NOM removal at each pH condition due to the increased Fe:DOC ratio. The influencing factor in NOM removal during these tests was seen to be coagulation pH and NOM removal mechanism.

The tests at coagulation pH 3.5 resulted in a system which was on the upper edge of the operational window for zeta potential and consequently had poor NOM removal performance. At pH 3.5 the likely interaction of the coagulant and NOM would have been patchwork agglomeration where only partial neutralisation is required to form floc (Ratnaweera *et al*., 1999) and the surface charge is not required to have been neutralized fully. The floc reformation factor was observed to increase in the more positive zeta potential systems on the outside of the operational window which suggests that patchwork agglomeration is an influencing factor in the floc reformation ability at this pH condition. At coagulation pH 6.5, some systems with more negative zeta potentials (<-10 mV) existed with sub-optimal NOM removal (>5 abs/m) and higher floc reformation factors than observed at pH 4.5. The mechanism for NOM removal at negative zeta potential values is thought to be due to polymer bridging between the high molecular weight material (Ratnaweera *et al*., 1999). The mechanisms of both polymer bridging and patchwork agglomeration could be said to be more supportive of floc reformation as reflected in the generally higher floc reformation values obtained at zeta potential >4 mV and zeta potential <-10 mV. The mechanism for NOM removal at pH 4.5 is reputed to be mainly charge neutralization (Duan and Gregory, 2002) which in these experiments consistently resulted in the lowest floc reformation factors. The data generated from these experiments wasn't comprehensive enough to fully substantiate the relationship between floc reformation and zeta potential as there were no systems with a zeta potential within the range -10mV to +2 mV. The results from Chapters 4 and 5 have substantiated the work of others such as Jarvis *et al.,* (2004) and Duan and Gregory (2002), and also expanded further to include the effects of operating outside of the literature quoted optimum pH for ferric salts of pH 4.5.

The impact of increasing Fe:DOC ratio on the dynamic flocculation parameters FI_{max}, floc strength factor and flocculation rate appear to be consistently linked. The most commonly changed parameter on a full-scale water treatment plant is the coagulant dose and therefore the Fe:DOC ratio, and it is useful to examine the effects of altering this key ratio on plant performance as a whole which is examined in Chapter 6.

Part 5.8 Conclusions

The experiments in this chapter were designed to investigate the inter-relationships between coagulation pH, Fe:DOC ratio, NOM removal and floc properties; and to establish the most suitable conditions for investigation at the pilot plant stage. The conclusions from the experiments were:

- At all coagulation pH conditions the relationship between FI_{max} and Fe:DOC was positive with a substantial impact as the ratio increased to 2.
- At coagulation pH 4.5 the increase in FI_{max} with Fe:DOC did not correspond to a decrease in floc strength factor suggesting that the flocs were more resistant to breakage despite their increased size – this suggests that it is possible to create larger flocs by increased Fe:DOC ratio without compromised breakage performance.
- Coagulation pH 4.5 was the most suitable pH throughout the dose range with respect to NOM removal.
- At coagulation pH 4.5 there was no effect of Fe:DOC on NOM removal despite increases in FI_{max} and a slight decrease in F_{ref} which suggests that there was no direct correlation with NOM removal and floc properties under these conditions.
- Systems with the highest R_{FI} did not always relate to the best performing system in terms of NOM removal, but were more sensitive to Fe:DOC ratio changes.
- At coagulation pH 6.5 the zeta potential data supported charge neutralisation as the coagulation mechanism, but the PDA readings was more supportive of "sweep" flocculation as the floc index was not representative of the floc size due to the large proportion of hydroxide. The conclusion is that operating at pH 6.5 at high Fe:DOC ratios was not conducive to producing good optical floc properties, and it is not suitable to monitoring with the PDA.
- Systems outside of the operational range of zeta potential tended to show improved floc reformation.
- Overall the results showed that increased FI_{max} corresponded with decreased floc strength factor.

It was concluded that there was no operational benefit to changing the coagulation pH, and the effects of substantially over-dosing coagulant relative to DOC were minimal with respect to NOM removal but did increase the floc size which may be beneficial for treatment and this aspect is studied next at pilot plant scale.

Chapter 6 The effect of Fe:DOC ratio on NOM removal, dynamic flocculation properties and filter performance using the DA20 pilot filtration plant

Part 6.0 Introduction

The pilot plant trials were carried out over a relatively long duration (3-4 months) in comparison to the jar tests in Chapters 4 and 5, these experiments were also carried out in summer rather than spring therefore raw water humic constituents may have been different. In these experiments the raw water was continually drawn from the main plant intake reservoir into the pilot plant, therefore any variability in the raw water quality would need to accounted for when analysing and interpreting the results. The experiments in Chapters 4 and 5 indicated that Fe:DOC ratio impacted on floc size (as quantified by FI_{max}) and these experiments sought to explore the effects on floc properties and NOM removal further, and furthermore to assess the impact of floc properties on filtered water quality and NOM removal. The impact of increased Fe:DOC ratio observed in the earlier jar tests presented in Chapters 4 and 5, tended to increase FI_{max} which could have an impact on filter performance as influent particle size is known to affect filtration processes to some extent.

The Fe:DOC range chosen for this set of experiments was relatively narrow within 0.7 – 1.2 which was thought to include both under-dosing and over-dosing, given that the literature quoted ratio of Fe:DOC for good removal is around 1 (Eikkibrook,1999; Vilge-Ritter *et al*., 1999; Cheng *et al*., 2002; Fearing *et al*., 2004). Another important aspect of this trial using the DA20 was to assess the viability of using the breakage jar test and PDA to measure the floc properties of water taken from the pilot plant static mixer; thus making the jar test a little more realistic with respect to the floc actually filtered on the pilot plant. The mixing unit on the DA20 was a static mixer, whereas the mixing method in the jar test was a paddle mixer; energy dissipation rates for the two types of mixing would have been different as completely different geometries. Although the conditions within the DA20 flocculators weren't replicated during the breakage jar tests, any disparity between initial mixing conditions was eliminated as it is known that initial mixing conditions have a large impact on floc size (Jarvis *et al*., 2005). The potential error between the Ferripol XL dose applied to the pilot plant through the dosing pumps, and dosing via pipette in the jar test was also removed.

Part 6.1 Raw Water Quality during DA20 Pilot-Scale Filtration Tests (May - August 2004)

The mean raw water quality during the trial period is tabulated in table 23, raw water pH was taken from the main plant online pH probes. The t-Test probability outcomes at the 95 percentile significance are also included for raw water variability comparison purposes between each run at the controlled Fe:DOC ratio condition. The data in table 23 shows that overall during the three month trial period the water quality was generally stable with respect to NOM content as measured by both DOC and UV_{254} absorbance. This was to be expected as operational experience has noted that the summer months are generally more stable with respect to NOM content; and this was thought to be due to lower rainfall/snow melt than winter or spring months. Raw water pH was very stable throughout the trial period but zeta potential was more variable, with 50% of the measurements exhibiting significant differences. The turbidity increased by approximately 50% between the first two trials, and the second two trials but was generally stable during the individual trials.

The mean SUVA for the raw water over the trial period was 3.6 m^{-1} L/mg C which was within the range for NOM-influenced coagulation, with a mixture of hydrophobic and hydrophilic components comprising the NOM (Edzwald and Tobiason, 1999). This was lower than the SUVA of the water used in the jar tests presented in Chapter 5 which was 4.9 m^{-1} L/mg C, and similar to that of batch 1 and 2 in Chapter 5 (3.7 m^{-1} L/mg C); but all were within a similar range of representative compounds according to (Edzwald and Tobiason, 1999).

Run No	Fe:DOC	Raw UV_{254} (abs/m)	Raw Zeta Potential (mV)	Raw Turbidity (NTU)	Raw DOC (mg/l)	SUVA (m -1 L/mg C)	Raw pH
1	0.7	30	-17.4	3.7	8.2	3.7	6.6
2	0.7	30	-15.4	4.7	8.4	3.6	6.6
3	0.7	29	-17.4	5.1	8.3	3.5	6.6
Mean		*30*	*-16.7*	*4.5*	*8.3*	*3.6*	*6.6*
S.E		*0.1*	*0.7*	*0.4*	*0.1*	*0.1*	*0*
1	0.8	34	-15.7	4.7	9	3.8	6.6
2	0.8	34	-15.6	4.6	8.8	3.9	6.6
3	0.8	33	-17.8	4.7	8.9	3.7	6.6
Mean		*33*	*-16.3*	*4.7*	*8.9*	*3.7*	*6.6*
S.E		*0.1*	*0.7*	*0*	*0.1*	*0.1*	*0*
1	1	30	-16.4	8.1	8.6	3.5	6.6
2	1	30	-16.1	8.2	8.6	3.5	6.6
3	1	31	-17.1	8	8.4	3.7	6.6
Mean		*30*	*-16.5*	*8.1*	*8.5*	*3.5*	*6.6*
S.E		*0.1*	*0.2*	*0*	*0*	*0.1*	*0*
1	1.2	30	-17.1	8.1	8.6	3.5	6.6
2	1.2	29	-16.4	8.2	8.9	3.3	6.6
Mean		*29*	*-16.7*	*8.1*	*8.7*	*3.3*	*6.6*
S.E		*0.1*	*0.4*	*0.1*	*0.2*	*0.1*	*0*
Ferripol XL dose (mg/l)	**Run Comparison**	**Probability outcomes at 95 percentile – Significantly different? Yes/No**					
0.7	1V2	No	**Yes**	**Yes**	No	No	No
0.7	1V3	No	No	**Yes**	No	No	No
0.7	2V3	No	**Yes**	No	No	No	No
0.8	1V2	No	No	No	No	No	No
0.8	1V3	No	**Yes**	No	No	No	No
0.8	2V3	No	**Yes**	No	No	No	No
1	1V2	No	No	No	No	No	No
1	1V3	No	No	No	No	No	No
1	2V3	No	**Yes**	No	No	No	No
1.2	1v2	No	No	No	No	No	No

Table 23 – Mean raw water quality measurements and T-test significant testing results during DA20 pilot scale filtration tests May –August 2004, Temperature 17°C, *Fe/DOC ratio in parentheses

Part 6.2 Pilot plant treated water quality during May-August 2004

The raw water was generally stable with respect to NOM content during the trial period, but was a little more variable with respect to turbidity and zeta potential. Zeta potential was the most variable parameter measured as determined by the significance testing at 95 percentile significance level. The treated water was therefore expected to reflect that variability, as the control parameter was Fe:DOC ratio not zeta potential. Table 24 contains the mean treated water quality during each control run.

The control runs at each Fe:DOC condition were compared using the t-Test at 95 percentile significance and the results are also shown in table 22. This data is the mean data calculated from the 6 hourly measurements obtained throughout the operation of the pilot scale trials. The filtration results are discussed separately as the filtration process is an inherently unsteady-state process whereas the primary treatment stages were intended to operate in a steady-state mode. The data in table 22 shows that zeta potential was the most variable parameter between the control runs and was also the more sensitive parameter to the controlled changes in Fe:DOC ratio.

Coagulation pH was controlled by manually adjusting the flowrate of lime suspension to achieve the desired pH as described in Chapter 3. This was carried out during the initial start-up phase when the DA20 plant was run to waste and not run to the pilot filter. There was some variability in the coagulation pH but this was not deemed significant as shown in table 24. The raw water zeta potential was also shown to be variable during the trials which may account for some of the variability in the treated water measurements. Overall the operation of the DA20 pilot-scale plant could be said to be reasonably stable and the following results regarding the effects of changing the Fe:DOC ratio on NOM removal, dynamic flocculation characteristics and filter performance; are thought to be representative of the influence of the main controlled parameter.

Run No	**Fe:DOC**	**Floted UV_{254} (abs/m)**	**Flocculated Zeta Potential (mV)**	**Floted Zeta Potential (mV)**	**Floted Turbidity (NTU)**	**Floted DOC (mg/l)**	**Coag pH**
1	0.7	5.3	-9.0	-6.9	1.3	1.3	4.6
2	0.7	5.3	-6.9	-8.4	0.9	1.5	4.5
3	0.7	5.6	-6.8	-10.7	1.0	1.7	4.4
Mean		*5.4*	*-7.6*	*-8.7*	*1.1*	*1.5*	*4.5*
S.E		*0.08*	*0.73*	*1.09*	*0.12*	*0.10*	*0.07*
1	0.8	6.4	-5.5	-5.1	1.5	1.4	4.6
2	0.8	6.7	-6.4	-4.9	1.2	1.5	4.5
3	0.8	6.4	-12.4	-12.2	1.4	1.9	4.6
Mean		*6.5*	*-8.1*	*-7.4*	*1.4*	*1.6*	*4.6*
S.E		*0.10*	*2.16*	*2.40*	*0.10*	*0.10*	*0.01*
1	1	2.5	-6.8	-8.1	1.0	1.2	4.6
2	1	2.6	-5.7	-8.8	1.0	1.2	4.5
3	1	2.2	-9.4	-9.6	0.9	1.0	4.5
Mean		*2.5*	*-7.3*	*-8.8*	*1.0*	*1.1*	*4.5*
S.E		*0.08*	*0.77*	*0.30*	*0.02*	*0.04*	*0.01*
1	1.2	4.0	0.8	-5.3	0.8	1.0	4.5
2	1.2	1.0	2.4	-2.7	0.9	0.6	4.6
Mean		*2.5*	*1.6*	*-4.0*	*0.9*	*0.8*	*4.5*
S.E		*1.52*	*0.80*	*1.33*	*0.20*	*0.19*	*0.01*
Fe:DOC	**Run Comparison**	**Probability outcomes at 95 percentile – Significantly different? Yes/No**					
0.7	1V2	No	Yes	Yes	No	No	No
0.7	1V3	No	No	Yes	No	No	No
0.7	2V3	No	No	Yes	No	No	No
0.8	1V2	No	Yes	No	No	No	No
0.8	1V3	No	Yes	Yes	No	Yes	No
0.8	2V3	No	Yes	Yes	No	No	No
1	1V2	Yes	Yes	No	No	No	No
1	1V3	No	Yes	Yes	No	No	No
1	2V3	Yes	Yes	No	No	No	No
1.2	1v2	Yes	No	Yes	Yes	Yes	No

Table 24 Treated water quality and control run comparison t-test results from DA20 pilot-scale dosing trials with variable Fe:DOC, May-August 2004, 17°C.

Part 6.3 Effect of Fe:DOC on floc properties

The dynamic flocculation curves generated from the breakage tests using the DA20 flocculator inlet water are shown in figure 61. The flocculation index trends were combined to give an average over the 5 tests during each experiment, and each experiment was repeated three times per trial with the exception of the final two trials. There were only 2 sets of PDA data generated during the 3rd and 4th trial as the PDA developed an electrical fault during the 3rd trial, and the DA20 scraper mechanism broke during the 4th trial thereby ending the experiment prematurely before the 3rd run at 1.2 Fe:DOC. The flocculation curves shown in figure 61 are therefore comprised of 50 sets of breakage jar tests, 15 sets each from trials 1 and 2 and 10 sets each from trials 3 and 4. The reproducibility was extremely good during each run at each condition and the results show a distinct and significant increase in FI_{max} as the Fe:DOC ratio was increased from 1 -1.2. In terms of Fe:DOC ratio, this increase in size was noted between the ratio of 1 to 1.2. There was no change in FI_{max} between 0.7:1 – 1:1 Fe:DOC.

Previous work by Jarvis *et al.* (2005) showed a similar pattern with respect to DOC:Fe ratio and floc size. They found that as the DOC:Fe ratio increased, the floc size decreased substantially due to the impact of the NOM preventing the primary particles from attracting and thus decreasing the floc size. Their work was carried out using a Mastersizer and the floc size reduction from a DOC:Fe ratio of 0:1 to 3.8:1 was recorded as 60%. They also noted a decrease in floc growth rate as the ratio of DOC:Fe increased, which was evident in figure 61 in this work. The initial period of floc growth was not visible on the flocculation curves as the jar test sample was taken from the pilot plant flocculator, and the floc was therefore already partially formed – the dynamic flocculation equipment was set up to reduce the transit time between pilot plant and jar test equipment. It was estimated that approximately 1 minute (time taken to fill jar and install in jar tester plus the residence time between static mixer and sample take-off) was missed off from the curves, which wasn't thought to be significant for the objectives of this trial. The maximum flocculation rate was not calculated in these experiments due to the initial period of floc formation being absent from the data and so qualitative comparison was used instead.

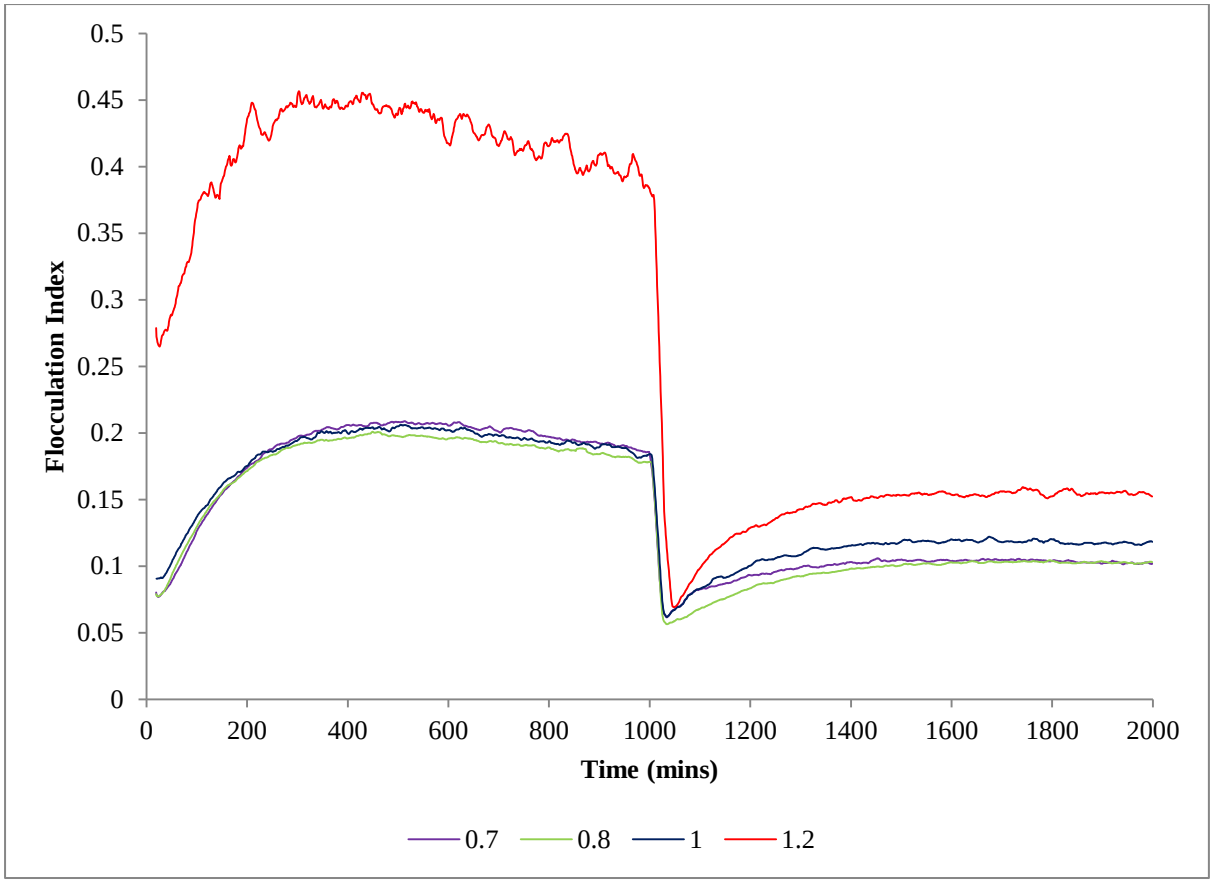


Figure 61 Mean dynamic flocculation curves during DA20 pilot-scale filtration tests using DA20 flocculator inlet water dosed to achieve Fe:DOC ratio 0.7-1.2, May –August 2004, 17 ° C

Table 23 shows the flocculation curve data derived from Table-Curve$_{TM}$ (with a r^2 of>0.9) from which the floc reformation factor and floc strength factor was calculated. Floc strength factor showed the same reverse trend with FI_{max} that has been observed in Chapter 5, as floc size increased the floc strength factor decreased. Floc reformation factor showed no obvious correlation with changes in Fe:DOC ratio, although the flocculation index at the end of the tests (FI_{ref}) showed an increase as FI_{max} increased. This suggests that the floc presented to the filter during the final trial using 11 mg/l Ferripol as Fe^{3+} was highly likely to have been considerably larger than the previous 3 trials which may have impacted on filter performance. The t-Test calculations in table 26 showed that there were no significant differences between the flocculation index data generated from the repeat control tests carried out during each experiment at the 95 percentile level. There is therefore considerable confidence in the consistency of the PDA generated flocculation index curves.

Ferripol XL Dose as Fe3+ (mg/l)	Fe/DOC ratio	Run no	FI_{max}	FI_{break}	FI_{ref}	Floc strength factor	Floc reformation factor
6	0.7	1	0.20	0.08	0.11	0.40	0.25
		2	0.22	0.08	0.12	0.36	0.29
		3	0.18	0.08	0.11	0.44	0.30
		Mean	*0.19*	*0.08*	*0.1*	0.40	0.28
		Standard Error	*0.01*	*0.02*	*0.01*	*0.02*	*0.01*
7	0.8	1	0.2	0.07	0.1	0.35	0.23
		2	0.2	0.08	0.12	0.40	0.33
		3	0.2	0.06	0.1	0.30	0.29
		Mean	*0.20*	*0.07*	*0.11*	0.35	0.28
		Standard Error	*0*	*0.006*	*0.007*	*0.029*	*0.030*
9	1	1	0.21	0.07	0.13	0.33	0.43
		2	0.19	0.04	0.12	0.21	0.53
		Mean	*0.2*	*0.06*	*0.13*	0.27	0.48
		Standard Error	*0.02*	*0.04*	*0.004*	*0.050*	*0.043*
11	1.2	1	0.48	0.07	0.16	0.15	0.22
		2	0.45	0.07	0.15	0.16	0.21
		Mean	*0.47*	*0.07*	*0.14*	0.15	0.22
		Standard Error	*0.01*	*0.01*	*0.02*	*0.005*	*0.004*

Table 25 – Mean dynamic flocculation performance parameters during DA20 pilot plant trials using flocculator inlet water and the breakage test, May-August 2004, 17 ° C

Fe:DOC	Run Comparison	FI_{max}	F_{brk}	F_{ref}	Different Yes/No?
0.7	1 v 2	1.51	0.51	0.21	No
0.7	1 v 3	0.95	0.42	0.95	No
0.7	2 v 3	0.42	0.78	0.98	No
0.8	1 v 2	0.56	1.11	2.54	No
0.8	1 v 3	1.11	0.66	2.14	No
0.8	2 v 3	0.37	0.24	1.02	No
1	1 v 2	1.25	0.24	0.35	No
1.2	1 v 2	0.36	0.25	0.12	No

Table 26 t-Test p values and outcomes at 95% significance level from comparison between control runs during dosing trial using Fe:DOC 0.7-1.2 and the breakage test on water originating from the DA20 pilot plant flocculator units.

Part 6.3.0 Inter-relationships between floc properties and NOM removal

Examination of the inter-relationships between the water quality parameters and the floc properties is best done by means of linear regression analysis to lend weight to identification of causal trends. This has been carried out using Excel$_{TM}$ regression function and the key correlation statistics relating to controlled changes in the independent variable Fe:DOC, and the dependent measured variables are displayed in table 27.

The significance is interpreted by using the t-Test probability value p as detailed in Chapter 3, if the result is <0.05 then the correlation can be deemed to be valid. The magnitude of the regression coefficient gives an indication of the effect of the dependent variable on the independent variable, or the strength of the correlation. The data set used for the initial review of the extent of correlations with the controlled or independent variable, was the hourly water quality measurements and dynamic flocculation data. Overall the results in table 27 indicate that there is a strong and significant relationship between:

- Fe:DOC and zeta potential (flocculated and floted)
- Fe:DOC and NOM removal (UV_{254} absorbance and DOC)
- Fe:DOC and floc properties (FI_{max} and F_{brk})

The outlier in this case was the correlation between Fe:DOC and floc reformation factor, which was very poor. Overall the data implies that there was a good relationship between the independent variable Fe:DOC ratio, and the dependent variables of water quality measurements and floc properties.

Independent Variable	**Dependent Variables**						
Fe:DOC	DOC removal (%)	UV_{254} absorbance removal (%)	Flocculated zeta potential (mV)	Floted zeta potential (mV	FI_{max}	F_{brk}	F_{ref}
Coefficient of regression r^2	0.88	0.72	0.71	0.65	0.71	0.99	0.01
t-Test p value	0.0212	0.0190	0.0111	0.0430	0.0428	0.0007	0.1716
Significant? Yes/No	Yes	Yes	Yes	Yes	Yes	Yes	No

Table 27 Regression statistics from correlations between Fe:DOC, floc properties and NOM removal using DA20 pilot plant hourly test data

This can then be expanded on to incorporate other correlations with floc properties having found that there were good correlations between the controlled variable and the measured variables. The results from which are shown in table 28 and 29. This data illustrates that the only parameter deemed to be significantly and strongly related to flocculated or floted zeta potential was FI_{max}. The NOM removal parameters of residual DOC and UV_{254} absorbance were found not to be significantly related to zeta potentials and mostly were weakly correlated.

Independent Variable	**Dependent Variables**				
Flocculated zeta potential (mV)	FI_{max}	F_{brk}	F_{ref}	DOC removal (%)	UV_{254} absorbance Removal (%)
Coefficient of regression r^2	1.00	0.78	0.29	0.70	0.40
t-Test p value	0.0014	0.3207	0.8388	0.3211	0.9821
Significant? Yes/No	Yes	No	No	No	No

Table 28 Regression statistics from correlations between flocculated zeta potential, floc properties and NOM removal using DA20 pilot plant hourly test data

Independent Variable	Dependent Variables				
Floted zeta potential (mV)	FI_{max}	F_{brk}	F_{ref}	DOC removal (%)	UV_{254} absorbance removal (%)
Coefficient of regression r^2	0.91	0.64	0.52	0.38	0.13
t-Test p value	0.001	0.4603	0.5112	0.6801	0.2332
Significant? Yes/No	Yes	No	No	No	No

Table 29 Regression statistics from correlations between floted zeta potential, floc properties and NOM removal using DA20 pilot plant hourly test data

Table 30 and 31 shows the data from a comparison of the NOM removal performance data sets and the floc properties; this shows that floc reformation factor and FI_{max} were poorly correlated with UV_{254} absorbance and DOC but correlation with floc strength factor was better. All three correlations were not found to be significant at the 95% confidence level. Overall this implies that the linkage between the NOM removal performance and the PDA derived floc properties was weak.

Independent Variable	Dependent Variables		
UV_{254} absorbance removal (%)	FI_{max}	F_{brk}	F_{ref}
Coefficient of regression r^2	0.35	0.66	0.10
t-Test p value	0.1182	0.9161	0.2770
Acceptable Yes/No	No	No	No

Table 30 Regression statistics from correlations between UV_{254} absorbance and floc properties using DA20 pilot plant hourly test data

Independent Variable	Dependent Variables		
DOC removal (%)	FI_{max}	F_{brk}	F_{ref}
Coefficient of regression r^2	0.28	0.45	0.00721
t-Test p value	0.2122	0.0901	0.5652
Acceptable Yes/No	No	No	No

Table 31 Regression statistics from correlations between DOC and floc properties using DA20 pilot plant hourly test data

Overall the regression analysis implies that there was a good correlation between Fe:DOC ratio, NOM removal performance and floc properties; with the exception of floc reformation factor. The zeta potential was found to correlate well and significantly with FI_{max} but not floc strength factor or floc reformation factor. However the analysis showed that the correlations between NOM removal performance and floc properties were not significant, and poorly correlated. This implies that either the linear model was incorrect, or there was no causal relationship. The regression statistics from analysis of the relationships between the floc properties is presented in table 32. The data implies that the correlation between FI_{max} and F_{brk} was reasonable and significant, but poor and insignificant between FI_{max} and F_{ref}.

Independent Variable	**Dependent Variables**	
FI_{max}	F_{brk}	F_{ref}
Coefficient of regression r^2	0.72	0.25
t-Test p value	0.0001	0.0910
Acceptable Yes/No	Yes	No

Table 32 Regression statistics from correlations between FI_{max} and floc strength and reformation factors using DA20 pilot plant hourly test data

Figure 62 illustrates the inverse effect of Fe:DOC ratio on floc strength factor, and the positive correlation with FI_{max}. This shows similar trends to those seen previously in Chapters 4 and 5. Floc strength factor was found to be inversely proportional to floc size. The correlation was strong and linear, and showed a decreasing trend with increased Fe:DOC ratio. This implied that the floc had less resistance to shear at the higher ratios because of its larger size, and more resistance at the lower ratios due to its smaller size. This was despite only a small increase in FI_{max} as the dose ratio increased from 0.7-1.

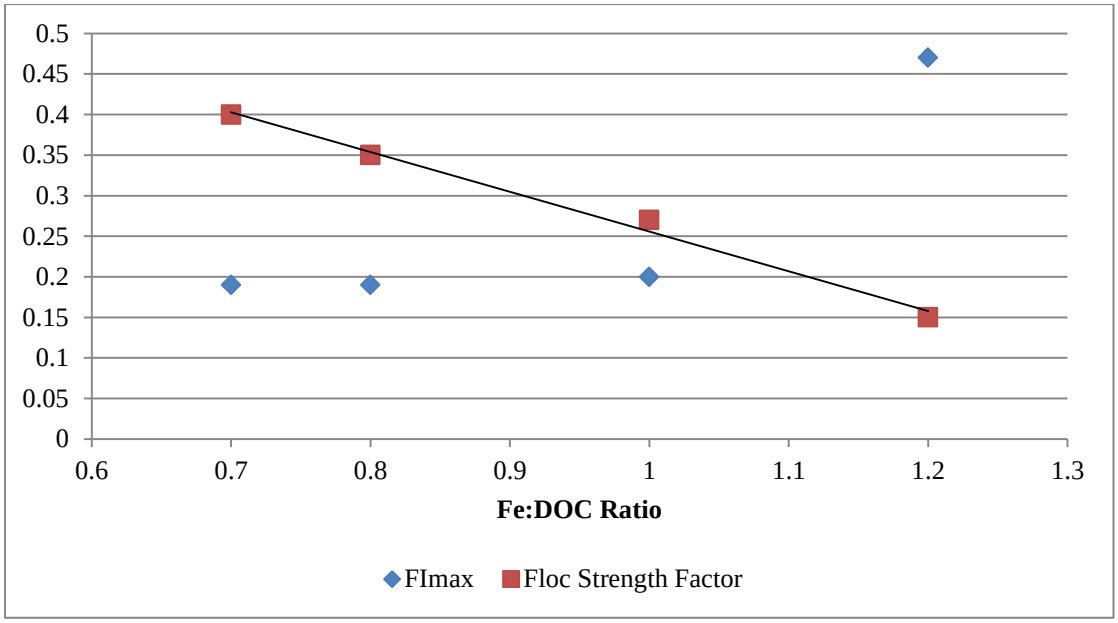


Figure 62 Relationship between Floc strength factor, FI_{max} and Ferric:DOC ratio during DA20 pilot plant trials using flocculator inlet water and the breakage test, May-August 2004, 17 ° C

Overall the regression statistics indicate that the most influential correlations were found between Fe:DOC and the measured parameters, with the exception of floc reformation factor. The strength of the correlation between zeta potential and FI_{max} was also notable which is contrary to the findings of Jarvis *et al.*(2004) who found no correlation between zeta potential and floc properties. The lack of correlation between the floc properties and NOM removal performance is counter-intuitive as Fe:DOC was found to impact on NOM removal, and was also found to relate to FI_{max}. Given that FI_{max} was found to correlate strongly with F_{brk} it is logical that a correlation between NOM removal and floc properties also exists; but this wasn't shown to be the case. The regression analysis results overall suggest that the Fe:DOC ratio is the most important parameter with respect to the floc properties. The lack of correlation shown between floc properties and NOM removal may have been due to the relatively narrow range of Fe:DOC ratios examined within the pilot plant trials.
Other studies by Jarvis *et al* (2004) used a much wider band of DOC:Fe of 0 to 4.8, and whilst they didn't report specifically on NOM removal they did note significant changes in floc structure as the DOC: Fe ratio increased.

Part 6.4 Effect of Fe:DOC ratio on zeta potential

Zeta potential has been shown in tables 23 and 24 to be a more variable parameter than the other water quality measurements recorded during this trial. The t-test results at the 95 percentile significance level show this to be the case. Figure 63 shows the mean zeta potential measured through the primary treatment stages during the four trials. Zeta potential is plotted against the mean Fe:DOC ratio which has already been shown to be correlated to dose. This shows that there was a general trend of increased flocculated and floted zeta potential as Fe:DOC ratio increased, with a more prominent increase noted at a Fe:DOC ratio of 1.2. There was also an appreciable and statistically significant difference in zeta potential between the flocculation and flotation stages, with the flotation measurements generally found to be more negative than the flocculated zeta potential readings.

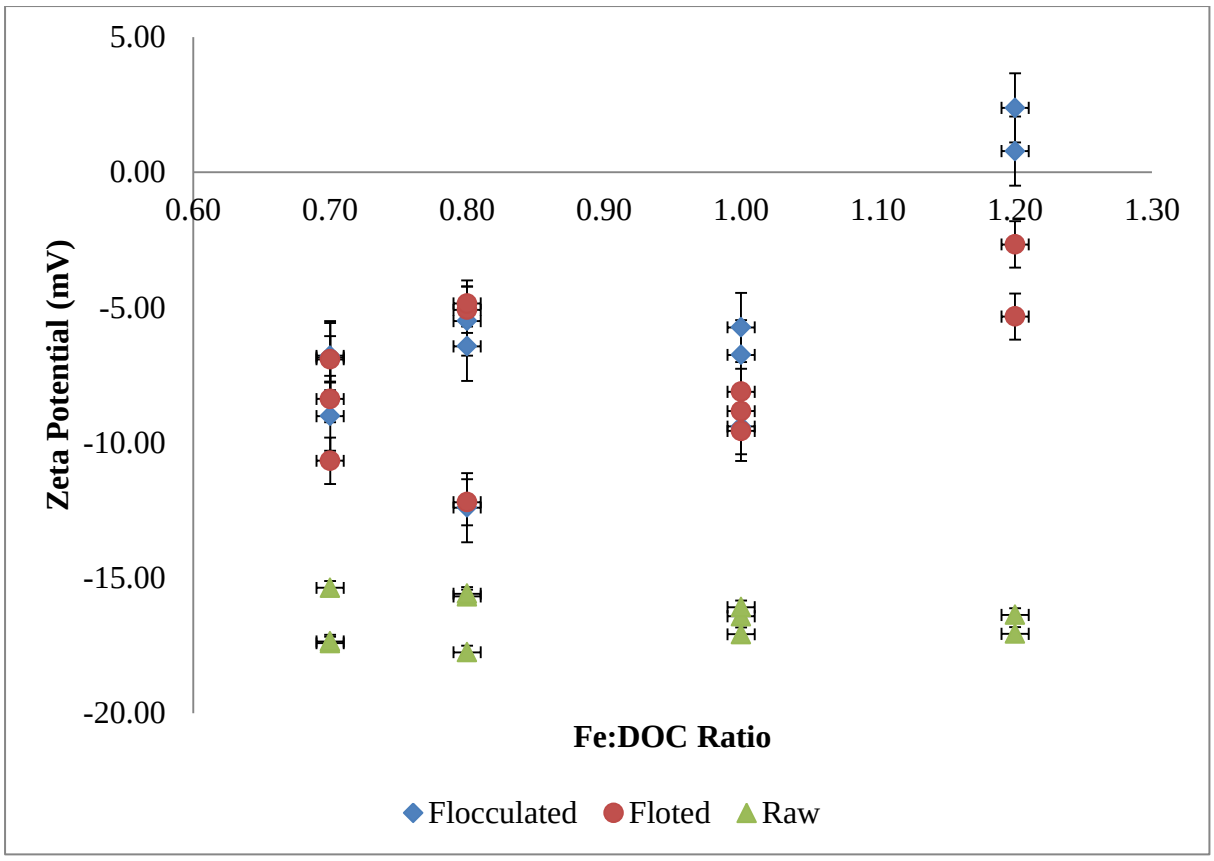


Figure 63 The effect of Fe:DOC ratio on flocculated and floted zeta potential. DA20 pilot-scale dosing trial May-August 2004, coagulation pH 4.5, 17°C

Table 33 shows the t-test results generated from comparing flocculated and floted zeta potential at the 95 percentile significance level. This shows that for 3 out of the 4 dosing trials, there was a significant difference and the significance of the difference increased as the Fe:DOC ratio increased. This implies that the flotation process had an impact on the surface charge of the floc as well as the buoyancy. Previous research has found that good flotation performance occurred when the bubble and particle were oppositely charged (Han and Kim, 2000; Jefferson, 1997). This points towards a mechanism by which flocculated zeta potential may impact on flotation efficiency. Presumably bubble zeta potential is relatively stable and therefore changes in flocculation zeta potential may impact on the collision efficiency of bubble and floc particle.

Mean Fe:DOC ratio	T-test probability factor p	Significant (Yes/No)
0.7	0.86	No
0.8	0.02	Yes
1	0.01	Yes
1.2	0.007	Yes

Table 33 t-Test probability factors and significance at 95 percentile significance level. Comparison of flocculated and floted zeta potential measurements during DA20 pilot-scale dosing trial, May-August 2004

A mechanism for explaining the decrease in zeta potential over the flotation process could be the effect of "air-stripping" on the poorly buffered soft water that is treated at Albert WTW. There are two potential locations which "air-stripping" can be carried out in the DAF unit:

1. Part of the DAF process consists of a packed tower containing pall rings which is used to facilitate mass transfer of air into the DAF outlet water. This produces the recycle stream which is fed to the nozzles at the bottom of the DAF tank. The recycle stream is typically 8% of the total flow of the flotation unit. It is possible that the process of dissolving the air into the water strips some of the CO_2 out of the water and thereby changes the zeta potential of the water in the recycle stream which has an impact on the entire tank.
2. The alternative location is within flotation tank itself. The incoming flocculated water is instantly met by a stream of micro-bubbles in the "contact zone" which may cause stripping of any CO_2 still dissolved in the water.

The author could find no previous reference to work specifically relating to the impact of the flotation process on zeta potential within the field of water treatment other that the work of Han and Kim (2000) which was focussed on the area of optimising collision efficiency. It would be beneficial to expand the research on this area to better understand the mechanism for the change in zeta potential and this is discussed further in Chapters 8 and 9.

Part 6.5 Effect of Fe:DOC ratio on NOM removal

The Fe:DOC ratio was gradually increased during this pilot-scale plant trial and the effect on the residual UV_{254} absorbance and DOC was monitored. The raw water quality with respect to both of these parameters was deemed consistent throughout the trial period. The resulting impact of increased Fe:DOC ratio on the residual UV_{254} absorbance and DOC was negligible during the first 2 trials, but then increased by approximately 10% as the Fe:DOC ratio increased from 0.8 to 1. The best performance was observed during the final trial using a Fe:DOC ratio of 1.2. The t-Test results at the 95 percentile level as shown in table 34, indicated that there were significant differences in residual NOM content between trials 1 to 3, but 3 and 4 were similar which is illustrated in figure 64. This shows the mean residual UV_{254} absorbance and DOC removal during each trial.

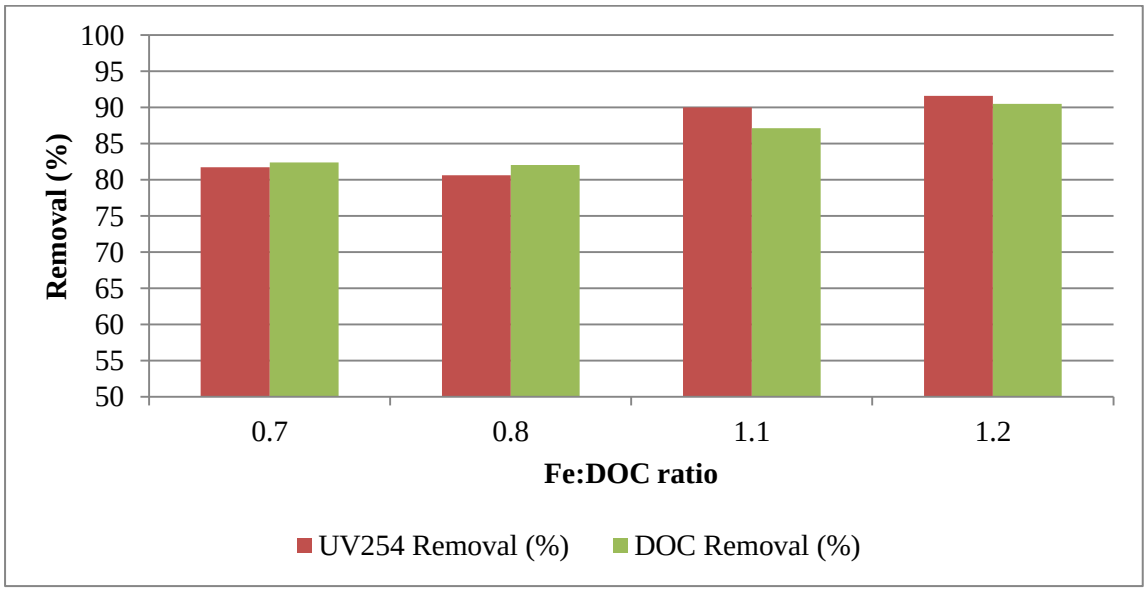


Figure 64 The effect of Fe:DOC ratio on mean UV_{254} absorbance and DOC removal during DA20 pilot-scale dosing trial May-August 2004, coagulation pH 4.5, 17°C

In terms of the final residual UV_{254} absorbance carried over to the filtration stage, the limit for minimising the risk of exceeding the final water THM limit was set to <5 abs/m at Albert WTW. This limit was met at a Fe:DOC ratio of 1 and 1.2 but was exceeded at the 2 lower ratios. The performance at Fe:DOC ratio of 0.7 and 0.8 was only just outside of the operating limit which suggests that at coagulation pH 4.5, this was on the edge of the operational window of for good performance. DOC measurements generally followed the same trend as the UV_{254} absorbance readings as would be expected although less variation was observed with this parameter. Table 24 shows that there were no significant differences observed in DOC between any of the control runs at each Fe:DOC ratio, but there were three differences noted as measured by UV_{254} absorbance. The most notable difference between the control runs was observed between the two runs carried out at Fe:DOC ratio of 1.2, where the difference in UV_{254} absorbance was very significant (3.99 and 0.95). This difference was not mirrored in the DOC measurements presumably due to differences between the techniques and their respective limits and sensitivities. Both measurements followed the same general trend throughout. Figure 65 shows a tendency towards decreasing residual UV_{254} absorbance as the floted water zeta potential approached zero. The operational window as specified by Sharp *et al.* (2006) was less obvious, as there were some high results (6-7 abs/m) observed within the operational window.

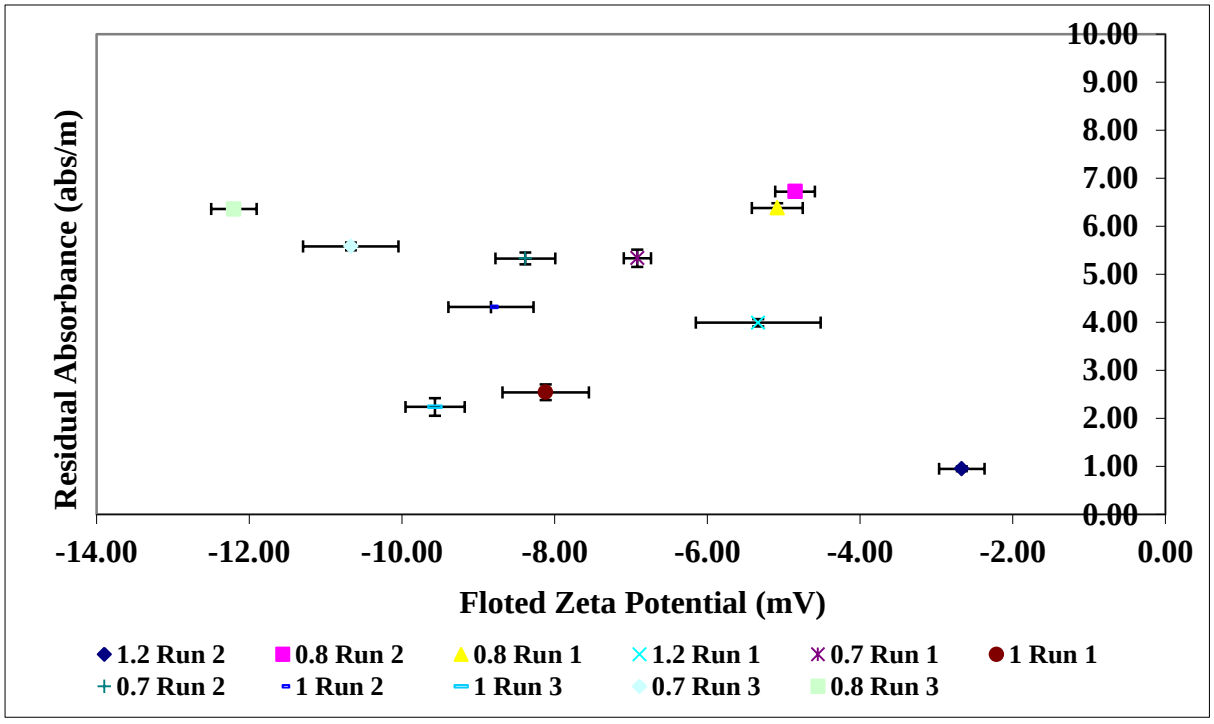


Figure 65 Residual UV_{254} absorbance and floted zeta potential during DA20 pilot-scale dosing trial May-August 2004, coagulation pH 4.5, 17°C

The operational window for zeta potential is more apparent in figure 66, with the most likely reason for this being the fact that Sharp *et al.* (2006) specified the window according to DOC and not UV_{254} absorbance. This may have been due to differences in the measurement accuracy of the UV spectrophotometer compared to the DOC analyser. The overall range of residual DOC was not as broad as would have been achieved if a wider range of Fe:DOC had been applied.

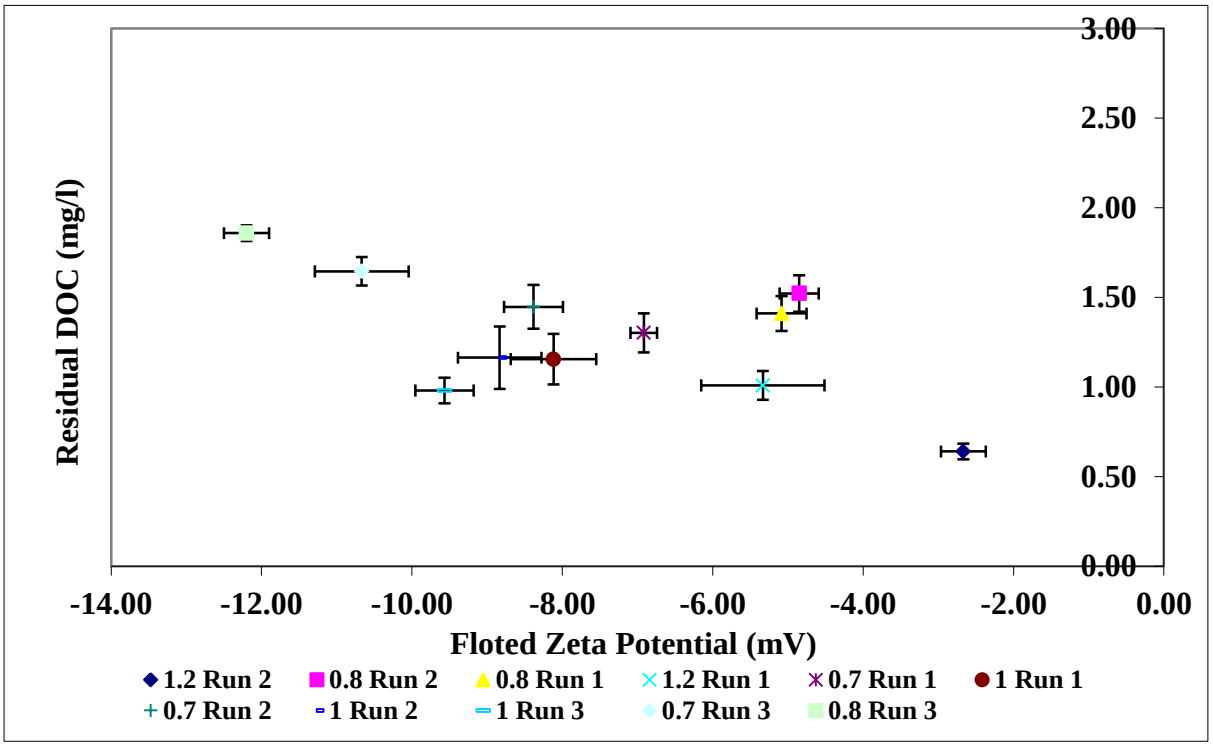


Figure 66 Correlation between residual DOC and floted zeta potential during DA20 pilot-scale dosing trial May-August 2004, coagulation pH 4.5, 17°C

Part 6.6 DA20 Floted Turbidity Measurements

Turbidity is another important measure of process performance and it is generally used as a surrogate control parameter for suspended solids that may contain pathogens such as cryptosporidium parvum oocysts. The expert report commissioned by DEFRA (Badenoch, 1995) formed the basis for setting turbidity limits to minimise the risk of passage of *cryptosporidium* through the process stages. The upper operational limit set at Albert WTW on the flotation outlet was 4 NTU and for filtration units was 1 NTU. Operating within these limits is considered to minimise the risk to an acceptable level; although in practice filtration units should be able to achieve turbidities <0.5 NTU during most of their filtration cycle.

During the dosing trial the raw water turbidity was consistent between the first two dosing trials but then significantly increased by approximately 40% during the remaining 2 dosing trials. The reason for the increase wasn't known exactly but could have been due to raw water pumping regime changes in the catchment. Figure 67 shows the mean raw and floted turbidity derived from the hourly measurements during the dosing trials. The floted turbidity measurements during the final trial were available online and so the mean was taken from the online measurements recorded at 1 min intervals during the 6 hour run duration. The performance of the pilot plant with respect to the operating below the limit of 4 NTU, was good and was well within the limit under all conditions. The floted turbidity performance was superior during the final trial using a Fe:DOC ratio of 1.2. The general trend observed was an improvement in performance as the Fe:DOC ratio increased. This was despite the increase in raw water turbidity.

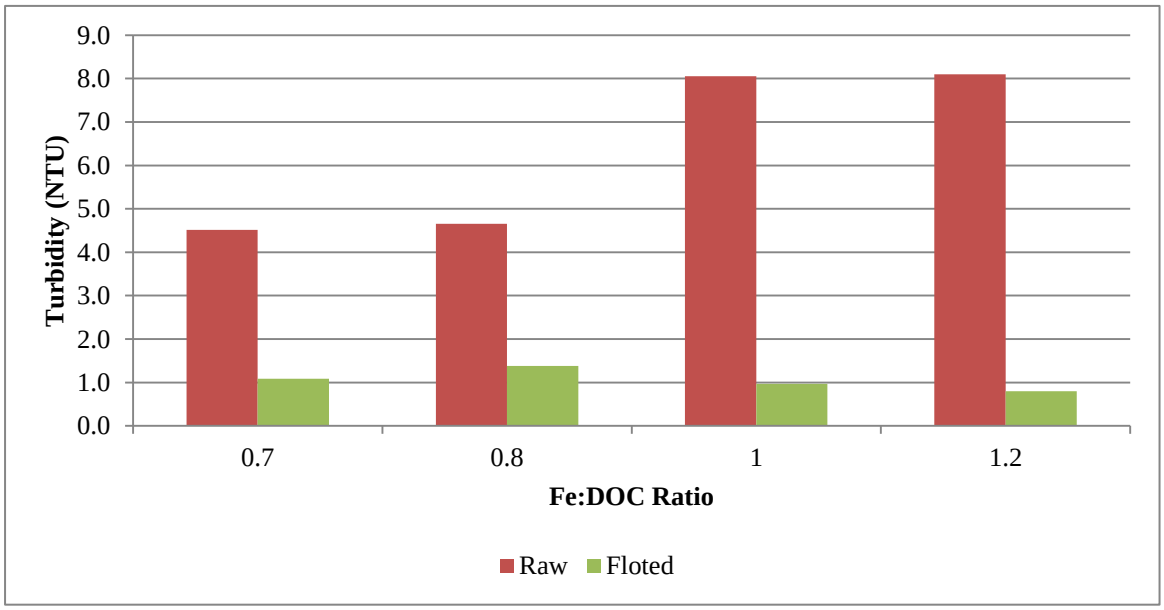


Figure 67 Mean raw and floted turbidity and Fe:DOC ratio during DA20 pilot-scale dosing trial May-August 2004, coagulation pH 4.5, 17°C

	Raw Water Parameters				**Treated Water Parameters**					
Dosing trial comparison	*UV_{254} absorbance*	*Turbidity*	*Zeta potential*	*DOC*	*UV_{254} absorbance*	*Flocculated zeta potential*	*Floated zeta potential*	*Floated turbidity*	*DOC*	*Coagulation pH*
1 v 2	1E-08	6E-01	6E-02	7E-05	4E-04	6E-01	5E-02	4E-03	1E-01	1E-1
1 v 3	1E-01	3E-13	5E-01	8E-02	5E-08	6E-01	6E-01	1E-01	5E-03	6E-1
2 v 3	6E-10	2E-17	2E-01	3E-02	5E-10	1E-01	9E-02	3E-05	#N/A	5E-1
1 v 4	5E-01	2E-10	2E-01	1E-02	9E-05	3E-08	3E-08	3E-02	2E-03	3E-1
2 v 4	1E-06	3E-12	1E-05	1E-01	1E-05	2E-07	2E-01	4E-02	1E-04	1E-1
3 v 4	1E-01	3E-15	4E-02	7E-01	2E-01	9E-07	3E-05	4E-01	3E-02	5E-1
	t-Test probability outcome. Different Yes/No									
1 v 2	Yes	No	No	Yes	Yes	No	No	Yes	No	No
1 v 3	No	Yes	No	No	Yes	No	No	No	Yes	No
2 v 3	Yes	Yes	No	Yes	Yes	No	No	Yes	Yes	No
1 v 4	No	Yes	No	Yes	Yes	Yes	Yes	Yes	Yes	No
2 v 4	Yes	Yes	Yes	No	Yes	Yes	No	Yes	Yes	No
3 v 4	No	Yes	Yes	No	No	Yes	Yes	No	Yes	No

Table 34 Raw and treated water t-Test probability factors(p) and outcomes from comparison of four DA20 dosing trials

Part 6.7 Effect of Fe:DOC ratio on filter performance using the DA20 pilot plant and pilot filtration column

Filtration is an inherently unsteady-state process and goes through distinct stages as shown in figure 3 in Chapter 2. The key filtration monitoring parameters monitored in the four trials were:

- Effluent turbidity and particle counts
- Headloss
- Flowrate

using online instruments where available, and the resulting trends are presented and discussed next. Headloss was not monitored online during the majority of the trials as the instrument wasn't configured – readings were instead taken from pressure gauges on an hourly basis whilst the online instrument was installed configured. The pressure gauges were installed at the same points (above and below the media) as the online pressure transmitter for consistency.

Part 6.8 Trial 1 filter performance using Fe:DOC ratio of 0.7

Part 6.8.0 Trial 1 Filter hydraulic performance at Fe:DOC ratio 0.7

There were two parameters measured that give indications of the hydraulic performance of the filter; declining flowrate and headloss. As stated in Chapter 3, the initial filtration rate was set to the same rate as the filters at Albert WTW which was 5.5 m/h. In practice, given that the filtration rate was manually adjusted to achieve the desired setpoint there was a little variation in the starting flowrates during each run. The variability between the three filtration rate and headloss trends was found not significant at the 95% confidence level as shown in table 35. This shows the comparison of the hydraulic parameters during the three runs at Fe:DOC of 0.7. For the statistical analysis, the headloss and filtration trends were compared using hourly data.

		Run 1	Run 2	Run 3
Filtration Rate	Starting filtration rate (m/h)	5.6	5.8	5.6
	Mean filtration rate (m/h)	5.5	5.6	5.5
	Rate of decline (m)	-0.0005	-0.0009	-0.0005
Headloss	Starting headloss (m)	0.22	0.22	0.23
	End headloss at 6 hours (m)	0.37	0.39	0.38
	Total headloss over run (m)	0.15	0.17	0.15
	Rate of increase in headloss (m/hr)	0.03	0.03	0.03
	Run comparison	Statistical Significance at 95% Significance level (Different Yes/No)		
Filtration Rate	1 v 2	P value = 0.11. No		
	1 v 3	P value = 0.82. No		
	2 v 3	P value = 0.12. No		
Headloss	1 v 2	P value = 0.15. No		
	1 v 3	P value = 0.42. No		
	2 v 3	P value = 0.24. No		

Table 35 Hydraulic performance of pilot filter during trial 1 using Fe:DOC 0.7

Part 6.8.1 Trial 1 Filtered water quality at Fe:DOC ratio 0.7

The filter performance during trial 1 is shown in figure 68. The particle count trend during run 3 was significantly different to that of the previous two runs, with the notable differences being the shape of the ripening curve, which was clearly defined in the trends from runs 1 and 2 but not in run 3. The turbidity trends showed very similar patterns during run 1 and 2, but a significant difference was observed in run 3 in terms of the ripening process. During run 3 the ripening part of the filtered turbidity trend was shallow in comparison to the other two runs. The turbidity trend during run 3 showed that the filter ripened eventually as a good baseline level was reached, but took considerably longer to achieve a steady-state filtrate quality compared to the other two runs which was reflected more in the particle count trend. The filtered water trends in run 3 showed that the turbidity trend was already showing ripening when the particle counts were increasing, which cannot be explained by differences in monitor location. The sample chamber within the turbidity monitor was larger in volume than the particle counter measuring chamber and therefore the residence time was longer in the turbidity monitor and would have been subject to a dilution factor.

The main reasons for the difference in filter effluent quality during run 3 could be attributed to the upstream processes. The UV_{254} absorbance and DOC measurements were very consistent between the three runs albeit higher than the operational standard of 5 abs/m. This indicated that the DA20 pilot plant was producing consistent quality water in terms of residual levels of humic substances. The turbidity data showed no significant differences between the three runs. The floted zeta potential however was significantly different between all three runs. The poor filter performance observed during run 3 could be attributed to the more negative floted zeta potential measured during this run. The floted water zeta potential during run 3 was -10.7 mV which is just outside of the operational window reported by Sharp *et al*. (2006).

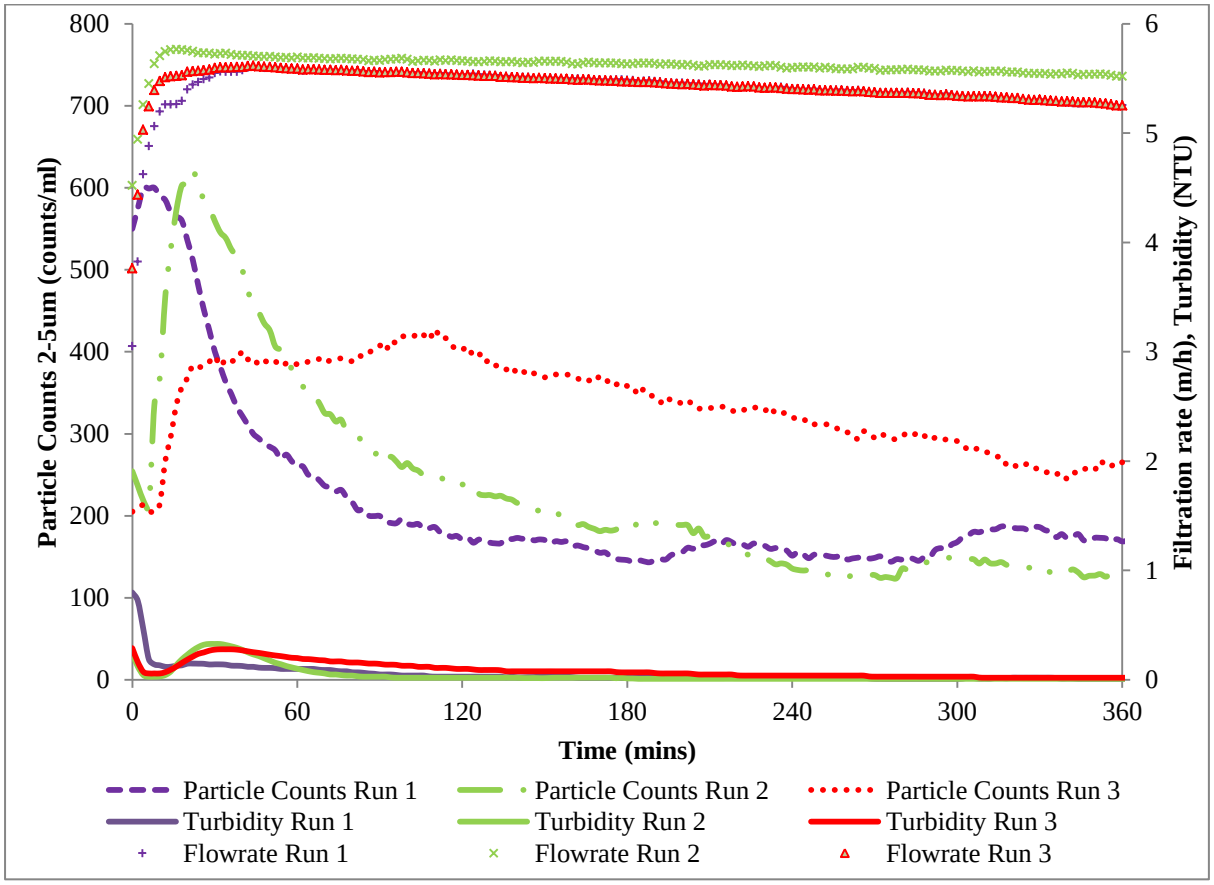


Figure 68 Filtered particle counts, turbidity and declining filtration rate trends at Fe:DOC ratio of 0.7 during DA20 pilot-scale dosing trial May-August 2004, coagulation pH 4.4-4.6, 17°C

This may have impaired the ripening process in particular and the general filtration process, as the charge was not well neutralised and this could have contributed to the poor performance of run 3 compared to runs 1 and 2.

The floted water zeta potential was within the operational window during runs 1 and 2 which overall performed better in terms of filtered water quality and ripening duration. The filtrate water quality as measured by turbidity was reasonably good during all three runs with each run producing water with a baseline turbidity of less than 0.1 NTU. According to the Badenoch report on minimizing the risk of cryptosporidium breakthrough (Badenoch, 1997); filtered water turbidity should be less than 1 NTU. The requirement for water quality presented to the disinfection stage is also less than 1 NTU to guarantee adequate destruction of pathogens. Taking this into account, the dose of 6 mg/l (Fe:DOC ratio 0.7) didn't perform as badly as expected, as it was considered to be an under-dose.

Part 6.9 Trial 2 filter performance using Fe:DOC ratio of 0.8

Part 6.9.0 Trial 2 Filter hydraulic performance at Fe:DOC ratio 0.8

Table 36 contains the data relating to the hydraulic performance of the filter. The statistical analysis performed on the hourly data of flow and headloss using the t-Test at the 95% confidence interval shows that there were no significant differences between the three filter runs. This implies that the hydraulic conditions were comparable between the three runs.

		Run 1	Run 2	Run 3
Filtration Rate	Starting filtration rate (m/h)	5.6	5.6	5.5
	Mean filtration rate (m/h)	5.4	5.3	5.3
	Rate of decline (m)	-0.001	-0.001	-0.001
Headloss	Starting headloss (m)	0.23	0.22	0.23
	End headloss at 6 hours (m)	0.40	0.40	0.40
	Total headloss over run (m)	0.17	0.18	0.17
	Rate of increase in headloss (m/hr)	0.03	0.03	0.03
	Run comparison	Statistical Significance at 95% Significance level (Different Yes/No)		
Filtration Rate	1 v 2	P value = 0.18. No		
	1 v 3	P value = 0.12. No		
	2 v 3	P value = 0.16. No		
Headloss	1 v 2	P value = 0.21. No		
	1 v 3	P value = 0.25. No		
	2 v 3	P value = 0.52. No		

Table 36 Hydraulic performance of pilot filter during trial 2 using Fe:DOC 0.8

Part 6.9.1 Trial 2 Filtered water quality at Fe:DOC ratio 0.8

Figure 69 illustrates the online filtered particle count and turbidity trends during runs 1-3 using Fe:DOC of 0.8. The effect of the periodic de-sludging of the flotation unit is clearly visible by the presence of small "humps" in the baseline particle counts, as was observed in the previous trial using 0.7 Fe:DOC. The effect of the de-sludging is less obvious in the filtered turbidity trends, which suggests that this measurement is less sensitive than particle counts. The particle count trends reveal slightly differing ripening trends; the trend observed during run 2 exhibited a faster ripening process than that in runs 1 and 3. The ripening patterns in all three particle count trends showed a shallow shoulder, and it is difficult to distinguish when the baseline quality was achieved, and if it completed ripening. Both turbidity and particle count trends show a small initial ripening peak thought to be due to intra-media remnants remaining from the backwash process. The filtered turbidity trend recorded during run 2 was not representative, as inspection of the turbidity monitor at the end of the run revealed that the measuring cell was very dirty and the lamp was covered in deposit thereby giving a falsely high and un-changing reading throughout this run.

The reason for this was due to the fact that the pilot filter had been run overnight using the floted water from the main plant, and this had unfortunately coincided with a coagulation pH failure which caused carryover of solids from the flotation units, and consequent fouling of the turbidity monitor measuring cell. The particle counter was unaffected because of the difference in the measuring cell arrangement. The turbidity monitor was cleaned out and normal operation was restored by the start of run 3. The turbidity and particle count trends recorded in runs 1 and 3 showed the presence of an intra-media remnants peak – which is usually an indication of insufficient backwash as the backwash should remove the deposits that have been dislodged from the media. The backwash procedure was not a variable in this study, and after each run the same procedure as described in Chapter 3 was performed. This phenomenon was also observed in trial 1. This implies that the period of water upwash at the end of the backwash could have been extended to improve the removal of the dislodged deposits.

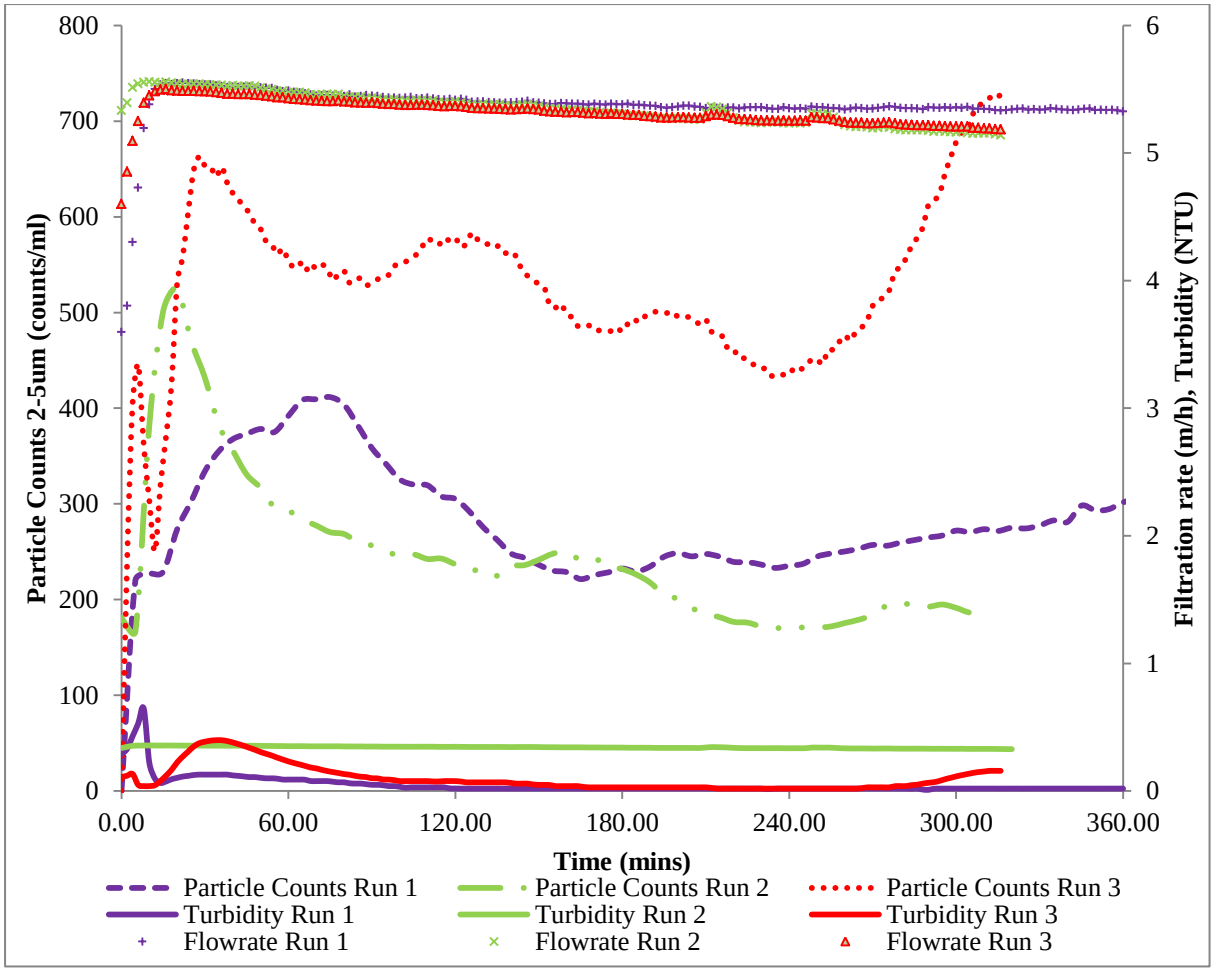


Figure 69 Filtered particle counts, turbidity and declining filtration rate trends at Fe:DOC ratio of 0.8 during DA20 pilot-scale dosing trial May-August 2004, coagulation pH 4.5-4.6, 17°C

The turbidity and particle count trend recorded in run 3 showed breakthrough in the final stages of the run. This was unusual as breakthrough was not usually associated with summer conditions at Albert WTW as filter breakthrough as illustrated in figure 1 in Chapter 1, is usually synonymous with winter conditions. The t-test results shown in table 24 show that there was a significant difference in zeta potential during run 3 (-12.2 mV) compared to the other two runs (-5.1 mV,-4.9 mV), which could be attributed to the more negative raw zeta potential during this run. This could have contributed to the filtered turbidity and particle count breakthrough observed at the end of run 3. It is important to note that the breakthrough in run 3 occurred at low headloss, and is therefore not thought to be as a result of an over-loaded filter.

All other treated water parameters weren't significantly different – the dynamic flocculation parameters that may relate to the breakthrough such as floc strength were not significantly different during run 3 as shown in table 25.

A reduction in floc strength factor was noted between runs 1-2, and run 3 but this was not shown to be significant. Residual DOC was slightly higher in run 3, but UV_{254} absorbance was consistent between the three runs. The residual UV_{254} absorbance was sub-optimal in all three runs, despite the floted zeta potential being within the operational window of -10 mV to +3 mV during run 1 and run 2. It is interesting that the residual UV_{254} absorbance was similar in run 3 to runs 1 and 2 considering the floted zeta potential was significantly lower during run 3. Trial 2 (run 3) results suggest that filter performance was very sensitive to zeta potential outside of the lower end of the operational window.

The turbidity and particle count trends indicated sub-optimal filter performance during all three runs, as the ripening duration was lengthy. On the full scale plant, the filter would be run to waste until the filtered turbidity reached a suitable level (usually less than 0.5 NTU), and this is normally achieved rapidly. The longer the filter is run to waste due to sub-optimal quality, the lower the overall efficiency of the treatment process. The baseline or steady-state filtration period was easy to identify in the turbidity trends, and reached a reasonable level in both runs 1 and 3.

Part 6.10 Trial 3 filter performance using Fe:DOC ratio of 1

Part 6.10.0 Trial 3 Pilot Filter hydraulic performance at Fe:DOC ratio 1

The hydraulic performance of the filter during trial 3 is summarised in table 37. Filtration rate and headloss trends over the filter run were not deemed to be significantly different during the three runs, and none of the three runs reached maximum headloss.

		Run 1	Run 2	Run 3
Filtration Rate	Starting filtration rate (m/h)	5.7	5.7	5.7
	Mean filtration rate (m/h)	5.5	5.5	5.5
	Rate of decline (m)	-0.0011	-0.0011	-0.008
Headloss	Starting headloss (m)	0.22	0.22	0.23
	End headloss at 6 hours (m)	0.40	0.40	0.40
	Total headloss over run (m)	0.18	0.18	0.17
	Rate of increase in headloss (m/hr)	0.03	0.03	0.03
	Run comparison	Statistical Significance at 95% Significance level (Different Yes/No)		
Filtration Rate	1 v 2	P value = 0.15. No		
	1 v 3	P value = 0.17. No		
	2 v 3	P value = 0.17. No		
Headloss	1 v 2	P value = 0.15. No		
	1 v 3	P value = 0.15. No		
	2 v 3	P value = 0.19. No		

Table 37 Hydraulic performance of pilot filter during trial 1 using Fe:DOC 1

Part 6.10.1 Trial 3 Filtered water quality at Fe:DOC ratio 1

The raw water parameters were consistent with the exception of zeta potential which was significantly different during run 3 compared to the other two runs. Figure 70 shows the online filter performance trends during each run. The headloss monitor was connected and operational during run 1 and run 3 during this trial but there was a fault during run 2.
The filtered particle count trends show that overall, the filter ripening sequence was more consistent between the three runs than was seen in the previous trials. The effect of the manual de-sludging of the flotation unit is apparent in the particle count trends shown in figure 70. All trends show small "humps" in the baseline that corresponded with de-sludging of the floatation unit. The presence of a small "backwash remnant" peak was also evident in the three runs as seen in the previous two trials.

It is difficult to determine from the trends in figure 70 whether the filtered particle counts showed true breakthrough at the end of the run as the small rises may have been due to de-sludging and not terminal breakthrough, but all three runs recorded an increase in particle counts towards the end of the run which was more pronounced during run 1. The turbidity trends don't show breakthrough during any part of the run. The zeta potential entering the pilot filter was within the operational window of –10 mV to +3 mV throughout the trial, and the filtered turbidity was <0.1 NTU for the majority of the filter run without breakthrough.

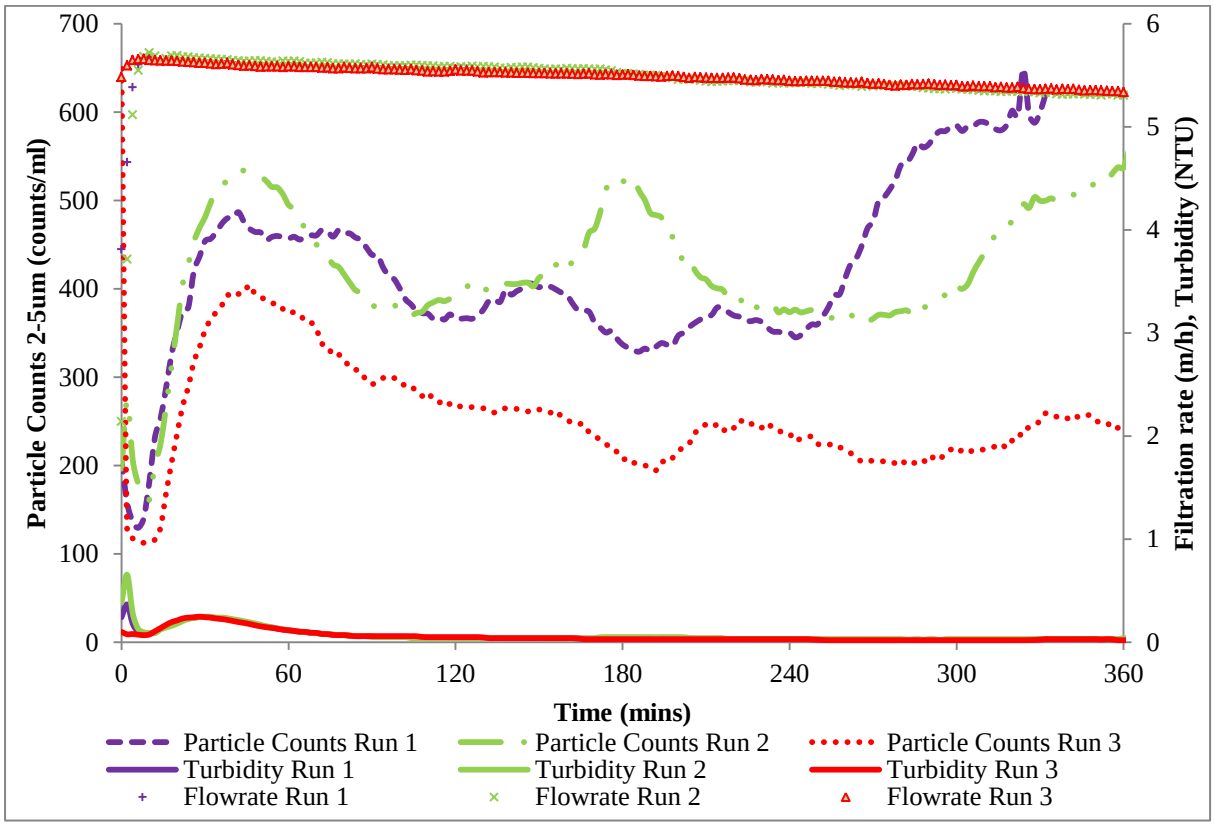


Figure 70 Filtered particle counts, turbidity and declining filtration rate trends at Fe:DOC ratio of 1 during DA20 pilot-scale dosing trial May-August 2004, coagulation pH 4.5-4.6, 17°C

Part 6.11 Trial 4 filter performance using Fe:DOC ratio of 1.2

Part 6.11.0 Trial 4 Pilot Filter hydraulic performance at Fe:DOC ratio 1.2

There were only 2 runs carried out under this condition as the DA20 flotation scraper mechanism broke at the end of the 2nd run and couldn't be repaired within the desired timescale.

The data in table 38 shows that unlike the other 3 trials, the floted UV_{254} absorbance and DOC were deemed to be significantly different between the 2 runs with the higher residuals observed during run 1. The reason for this difference is unaccounted for as the raw water was not found to be significantly different, and neither was coagulation pH or dose. The runs were carried out on consecutive days and neither the weather conditions or raw water source were noted to have changed.

		Run 1	Run 2
Filtration Rate	Starting filtration rate (m/h)	5.8	5.9
	Mean filtration rate (m/h)	5.5	5.5
	Rate of decline (m)	-0.0019	-0.007
Headloss	Starting headloss (m)	0.22	0.23
	End headloss at 6 hours (m)	0.32	0.33
	Total headloss over run (m)	0.10	0.10
	Rate of increase in headloss (m/hr)0.03	0.02	0.02
	Statistical Significance at 95% Significance level (Different Yes/No)		
Filtration Rate run 1 v run 2	P value = 0.0001. Yes		
Headloss run 1 v run 2	P value = 0.18. No		

Table 38 Hydraulic performance of pilot filter during trial 4 using Fe:DOC 1.2

Part 6.11.1 Trial 4 Filtered water quality at Fe:DOC ratio 1.2

Figure 71 illustrates the pilot filter performance trends during each run. Run 1 showed a higher particle count than run 2 at the start of the ripening period, but then reduced very quickly to a baseline level. In Run 1 the intra-media remnants peak was thought to be responsible for the high starting particle counts and turbidity. Run 2 exhibited a smaller ripening particle count which extended for a longer duration into the filter run than run 1. Both particle count baseline levels were reasonably stable during both runs. The particle count baseline was improved from the previous trials, thereby suggesting that filter performance was better. During this trial, a Great Lakes turbidimeter (same model as the filter outlet monitor) was connected to the flotation outlet so that the full real-time trend could be compared to the filter performance trends. Both flotation outlet turbidity readings were subject to “spikes” that coincided with de-sludging of the flotation unit, but neither appeared to impact directly on filtered turbidity or particle counts.

Overall filtration performance was good using Fe:DOC ratio of 1.2 as the filtered turbidity baseline levels were <0.1 NTU, and neither the filtered particle counts or turbidity exhibited breakthrough at any point during the runs.

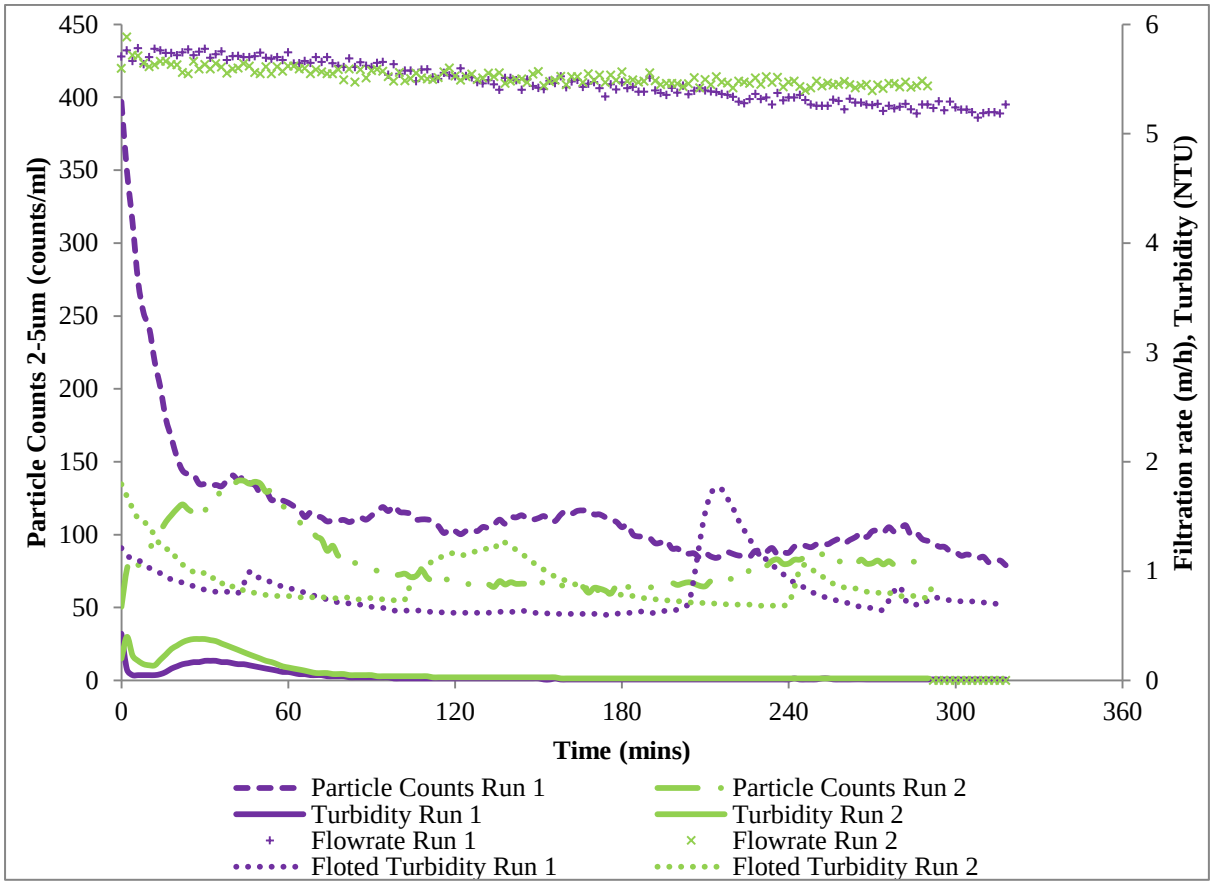


Figure 71 Filtered particle counts, turbidity, declining filtration rate and floted turbidity trends at Fe:DOC ratio of 1.2 during DA20 pilot-scale dosing trial May-August 2004, coagulation pH 4.5-4.6, 17°C

Part 6.12 Summary of filter performance

Part 6.12.0 Hydraulic filter performance summary and discussion

Hydraulic performance can be discussed in terms of both headloss and filtration rate, both of which are inter-linked. The pilot plant was set up to operate in declining flow mode and as such the filtration rate was expected to decline as the run progressed due to the increasing collection of particulate within the filter pores. The four filter trials were carried out in triplicate, with the exception of trial 4 which was only duplicated due to the failure of the scraper mechanism on the DA20. The hydraulic conditions at the start of the filter run were intended to be comparable as it is known that the filtration rate has an impact on the duration of the filter ripening sequence (Suthaker *et al.*, 2008).

For the relatively short filter runs undertaken in this study, it was of importance to ensure that the starting conditions were as comparable as possible. The manual operation of the filter outlet valve lead to some differences in the time taken to achieve the starting filtration rate, and in order to fully establish the significance of the differences in the starting filtration rates between the four trials a t-Test was carried out on the data. The results which are tabulated in table 39 show that overall there was only 1 case of significant difference in both the mean starting filtration rate, and the mean filtration rate. The significant difference found was between trial 2 and 3, which was caused by higher starting filtration rates and also higher mean filtration rates in trial 3 compared to 2. Comparison of the rate of flow decline between the four dosing trials is also included in table 39. The statistical comparison at the 95% confidence level shows that there was overall no significant difference in this parameter throughout the trial. Overall the headloss measurements such as the rate of increase in headloss were also found not to be significantly different between the four dosing trials. The starting headloss was also similarly comparable between the four trials which indicated that the backwashing procedure carried out between each filter run was adequate enough to clean to filter. If the backwashing was inadequate, over time it would be expected to see the starting headloss rise as the media would contain more deposits which have not been backwashed out. This was not shown to be the case. The headloss at the end of the run was well below the terminal headloss of 3.15 m, which was the total headloss possible through the filter column as shown in Chapter 3. This suggests that the filter was not significantly loaded, which is reasonable given that the pilot plant filter runs were much shorter than the main plant which was operating 24 hour run times and washing on time, rather than quality or headloss during this period.

The filter bed depth was half the depth of the main plant filters, therefore the pilot filter runs should have lasted at least 12 hours before resulting in significant headlosses or deteriorating quality. Overall the statistical analysis of the pilot filter hydraulic performance measurements shown in table 39 indicates that the impact of increased Fe:DOC ratio on the rate of flow decline and build-up of headloss was not significant. Given that the increase in Fe:DOC ratio was mostly found to correspond with a significant reduction in the floted turbidity, it is slightly counter-intuitive that this did not impact on the hydraulic performance of the filter.

Turbidity is not a surrogate parameter for solid flux rate however, so it is not possible to say whether the filter loading was different throughout the dosing trial as the relative dose of coagulant was increased. The impact of increased Fe:DOC ratio on filtered water quality in terms of turbidity and particle counts is discussed next.

Trial Comparison	1 v 2	1v 3	1 v 4	2 v 3	2 v 4	3 v 4
Starting filtration rate P value	0.08	0.53	0.10	0.0005	0.11	0.32
Significant (Yes/No)	No	No	No	Yes	No	No
Mean filtration rate P value	0.10	0.81	0.56	0.02	0.15	0.25
Significant (Yes/No)	No	No	No	Yes	No	No
Rate of decline in flow P value	0.1	0.08	0.37	0.39	0.37	0.22
Significant (Yes/No)	No	No	No	No	No	No
Starting Headloss P value	0.42	0.42	0.42	0.42	0.42	0.42
Significant (Yes/No)	No	No	No	No	No	No
End Headloss P value	0.21	0.23	0.42	0.41	0.42	0.39
Significant (Yes/No)	No	No	No	No	No	No
Rate of increase in headloss P value	0.08	0.06	0.23	0.42	0.42	0.41
Significant (Yes/No)	No	No	No	No	No	No

Table 39 t-Test P values and significance from comparison of pilot filter hydraulic performance parameters (starting filtration rate, mean filtration rate, rate of flow decline) between four DA20 dosing trials

Part 6.12.1 Filtered water quality summary and discussion

Table 40 shows a statistical comparison of the filtered particle counts and turbidity at the end of each filter run (t = 320 mins) using the t-Test at the 95% confidence level. This shows that whilst there was no significant difference in the final turbidity between the filter runs during each trial, there was a significant difference in the final particle counts measured during trial 4 and the rest of the three trials. The filtered water particle counts were found to be significantly lower during the 4th trial using 1.2 Fe:DOC.

Trial Comparison	1 v 2	1v 3	1 v 4	2 v 3	2 v 4	3 v 4
Filtered turbidity P value	0.51	0.50	0.48	0.49	0.28	0.41
Significant (Yes/No)	No	No	No	No	No	No
Filtered particle counts P value	0.20	0.33	0.02	0.86	0.03	0.04
Significant (Yes/No)	No	No	Yes	No	Yes	Yes

Table 40 t-Test P values and significance testing at the 95% level from comparison of pilot filter effluent turbidity and particle counts between four DA20 dosing trials

Filter breakthrough as measured by turbidity or particle counts signifies that the filtrate quality has deteriorated and the risk of passage of pathogens such as *Cryptosporidium* has increased. The filtered turbidity trends shown in figure 69 present clear evidence of premature filter breakthrough nearing the end of run 3 using 0.8 Fe:DOC. This was the only filter run to exhibit this trait, which given that the hydraulic conditions have been found to be comparable, is likely to be related to the influent water quality. In this run the floted water zeta potential of -12.2 mV was noted to fall below the bottom of the operational window for good NOM removal. This was therefore thought to be a likely contributor to the poor filter performance, given that zeta potential has previously been found to correlate with filter performance (Logsdon *et al.*, 2002). The exact mechanisms for the breakthrough weren't proven in this study but further research in this area would be extremely useful and is discussed further in Chapter 9.

The floc strength factor during run 3 using 0.8 Fe:DOC was not found to be significantly different compared to runs 1 and 2, and so it is difficult to attribute the filter breakthrough to a reduction in floc strength factor during this run. Floted water zeta potential was noted to vary significantly throughout the trial, and in some cases between individual control runs during trials. It is therefore interesting to evaluate the filtrate quality alongside zeta potential. The filtered turbidity measurements at the end of each run (t = 320 mins) are plotted against the mean floted zeta potential measurements during the four trials in figure 72. The results from run 2 during trial 2 have been omitted due to the dirty measuring cell and a falsely high result. The data shows a general decrease in filtered turbidity as the zeta potential approached zero. Realistically the range of turbidity measurements observed was within a narrow band for most filter runs and at the lower end of the monitor range – and were also not found to be significantly different throughout the trial as a whole. The best filter performance in terms of filtered turbidity is not easy to determine as the data is very close together and mainly within a narrow band of 0.01-0.03 NTU.

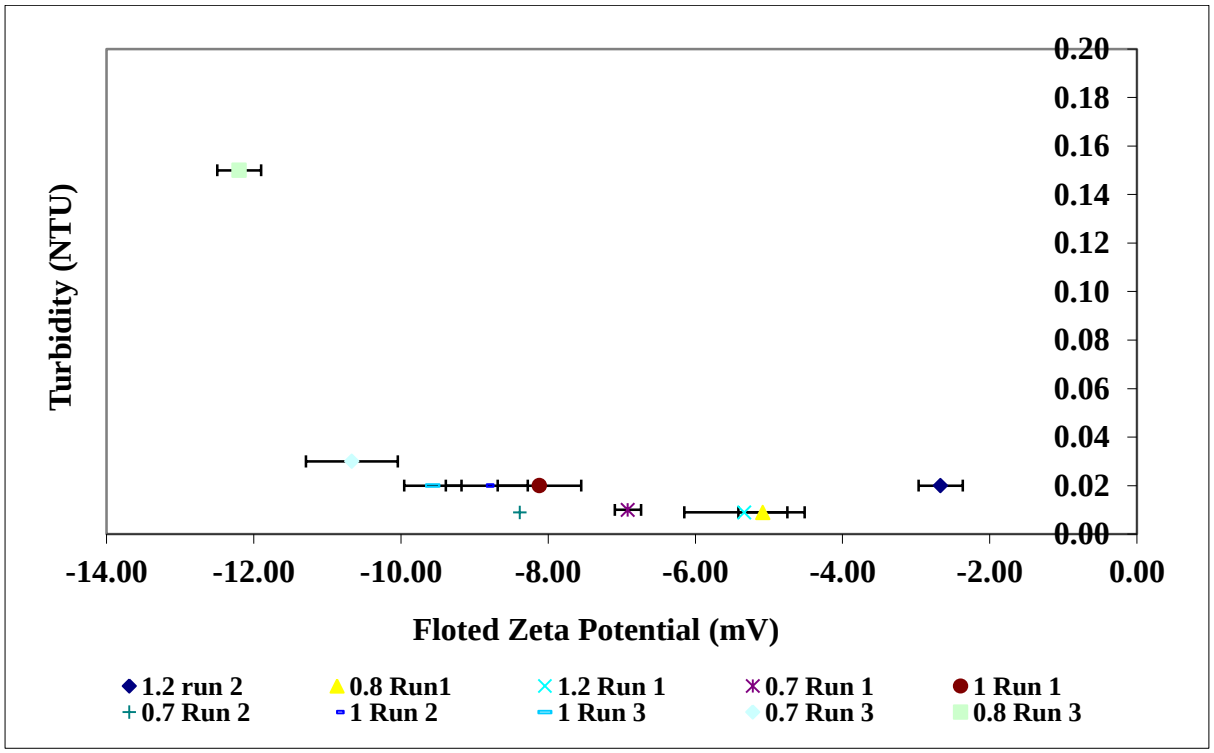


Figure 72 The effect of Fe:DOC on filtered turbidity at 320 mins and floted zeta potential during DA20 pilot-scale dosing trial May-August 2004, coagulation pH 4.5, 17°C

The particle count trends shown in figure 73 plotted against floted zeta potential also shows the same general trend as the turbidity trend in figure 72. This is expected as turbidity and particle counts generally followed the same patterns during the runs, albeit with a heightened sensitivity exhibited in the particle count measurements. There is no designated "safe" limit for particle counts as has been inferred with turbidity, but figures 72 and 73 show that the risk of passage of pathogens such as *Cryptosporidium* was greatly reduced as the zeta potential approached zero. Overall taken together figures 72 and 73 present compelling evidence that there is an operational window for zeta potential that corresponds with good filtrate quality; and performance is superior as the zeta potential tends towards 0 mV. This suggests that it should be possible to tailor coagulant dose to achieve a zeta potential within the operational range rather than tailoring coagulant dose to achieve a good residual UV_{254} absorbance; providing that there is a good correlation between the two parameters as has been observed to be the case in this work and by Sharp *et al.* (2006). Considering the particle count and turbidity data in figures 72 and 73, the best filter effluent quality was achieved using Fe:DOC of 1.2, which also corresponded to the lowest residual humic substances; and the highest floted zeta potential.

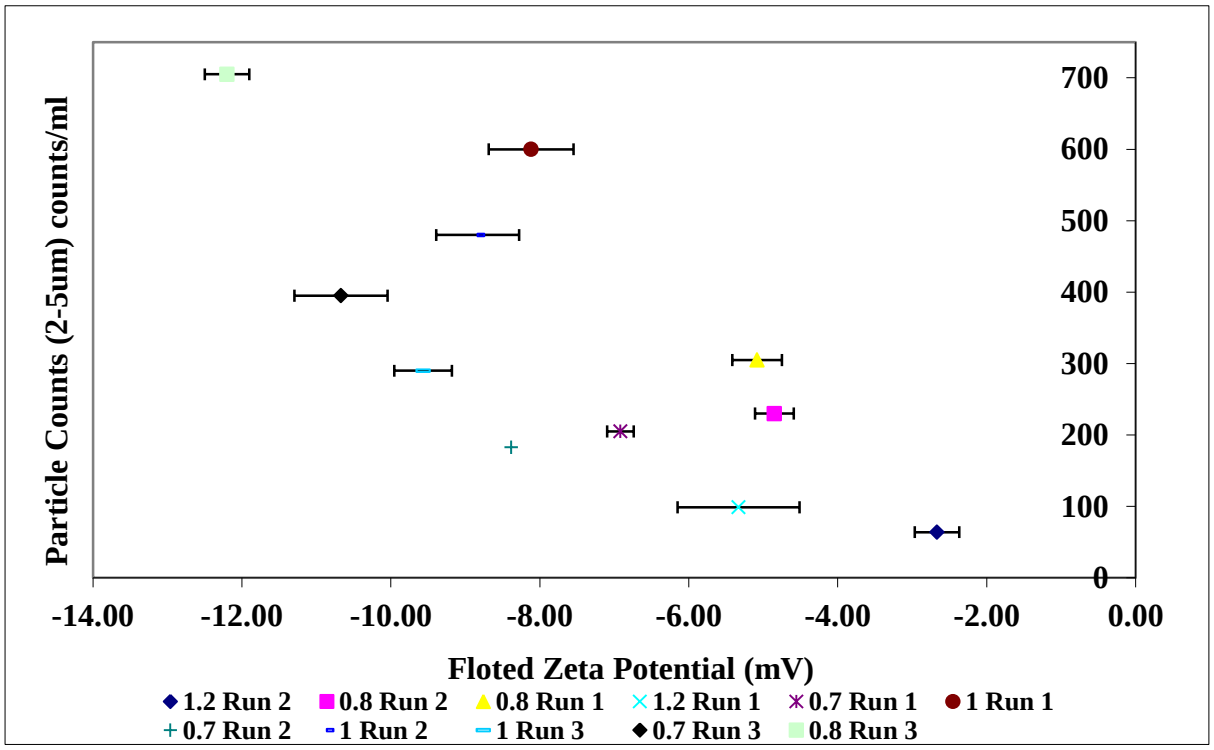


Figure 73 The effect of Fe:DOC on filtered particle counts at 320 mins and floted zeta potential during DA20 pilot-scale dosing trial May-August 2004, coagulation pH 4.5, 17°C

Part 6.12.2 Floc properties, filter performance and NOM removal summary and discussion

One of the objectives of this dosing trial was to correlate floc properties with NOM removal and filter performance, and improve understanding of changes in floc properties that cause filter breakthrough at low headloss. In this experimental work both surface charge and floc size were affected by changes in the controlled parameter Fe:DOC. It is therefore difficult to separate out the individual impacts of the effects of surface charge and floc size on filter performance without further analysis. Statistical analysis using the regression technique in Excel$_{TM}$ can be used to compare the significance and strength of the relationships. Table 41 shows the p-values and regression coefficients generated from this technique. This shows that the 2 significant correlations (with p value <0.05 at the 95% level) were between floted zeta potential and filtered particle counts, and FI_{max} and filtered particle counts. The correlation statistics between the floted zeta potential and filtered particle counts datasets returned a lower p-value, and a higher coefficient of regression. This implies that the relative impact of surface charge on filtered particle counts is greater than the impact of floc size as measured by FI_{max}. The remaining correlations were found to be statistically insignificant at the 95% significance level.

Correlation	p-value	R^2	Significant (Yes/No)
FI_{max} and filtered turbidity	0.54	0.06	No
FI_{max} and filtered particle counts	0.04	0.53	Yes
F_{ref} and filtered turbidity	0.85	0.10	No
F_{ref} and filtered particle counts	0.11	0.35	No
F_{brk} and filtered turbidity	0.82	0.008	No
F_{brk} and filtered particle counts	0.32	0.16	No
Floted zeta potential and filtered turbidity	0.09	0.4	No
Floted zeta potential and filtered particle counts	0.02	0.6	Yes

Table 41 p values and coefficients of regression generated in Excel$_{TM}$ from regression analysis between floc properties, zeta potential and filtered water quality. Analysis performed using pilot plant hourly data.

The results of the multi-variable regression using Excel$_{TM}$ to analyse the zeta potential, floc properties and NOM removal data-sets is shown in table 42. As Fe:DOC has already been shown to be strongly correlated with FI_{max} throughout this work, the multi-variable regression test is used to test the relationships as a whole using FI_{max} as the independent variable by use of the F-test statistic and the mean values from each individual dosing trial (the dependent variables). The data in table 42 shows that at the 95% significance level the p-value of the F-test is >0.05 and so the null hypothesis can't be rejected and it can be said that the dependent variables are not contributing to the regression model as a whole.

	Degrees of freedom	Sum of squares	Mean sum of squares	F	Significance F	
Regression	4	0.09	0.02	5.34	0.07	
Residual	4	0.02	0.00			
Total	8	0.11				
	Coefficients	Standard Error	t Stat	p-value	Regression Statistics	
Intercept	-2.75	1.13	-2.43	0.03	Multiple R	0.92
DOC Removal	0.04	0.02	2.48	0.02	R Square	0.84
UV_{254} Removal	-0.01	0.01	-0.88	0.43	Adjusted R Square	0.68
Floted zeta potential	-0.03	0.02	-1.37	0.24	Standard Error	0.07
Filtered particle counts	0.00	0.00	-1.88	0.13	Observations	9

Table 42 Results from Excel$_{TM}$ regression analysis generated from correlations between FI_{max} and DOC removal, UV_{254} absorbance removal, floted zeta potential and filtered particle counts. Analysis performed using mean data from individual runs.

Table 43 shows the results from the multi-variable regression analysis using filtered particle counts as the independent variable. This shows that as seen in the previous example, the data shows that at the 95% significance level the p-value of the F-test is <0.05. This means that the null hypothesis is rejected and it can be said that the dependent variables are contributing to the regression model as a whole. The individual contributions to the regression model are deemed significant with respect to floted zeta potential, but the remainder of the contributions of the independent variables was not deemed significant.

	Degrees of freedom	Sum of squares	Mean sum of squares	F	Significance F	
Regression	4	337225.04	84306.26	5.67	0.04	
Residual	4	59508.24	14877.06			
Total	8	396733.28				
	Coefficients	Standard Error	t Stat	P-value	Regression Statistics	
Intercept	-4714.82	2287.77	-2.06	0.11	Multiple R	0.92
DOC Removal	-1264.21	672.51	-1.88	0.13	R Square	0.85
UV_{254} Removal	60.60	38.07	1.59	0.19	Adjusted R Square	0.70
FI_{max}	-4.95	15.78	-0.31	0.77	Standard Error	121.97
Filtered particle counts	-84.16	26.38	-3.19	0.03	Observations	9

Table 43 Results from Excel$_{TM}$ regression analysis generated from correlations between floted zeta potential and filtered particle counts, FI_{max}, DOC removal, and UV_{254} absorbance removal. Analysis performed using mean data from individual runs.

The statistical analysis by means of the multi-variable regression helps to establish the contributions from the different independent variables on the dependent variables. The data overall shows that FI_{max} was not significantly related to the extent of NOM removal, zeta potential or filtered particle counts as a whole, and the individual correlations also confirm this to be true relative to NOM removal and charge. The multi-variable regression correlation between floted zeta potential and NOM removal, FI_{max} and filtered particle counts did prove significant as a whole. The most influential parameter in this case was found to be filtered particle counts. Overall this suggests that the influence of zeta potential on NOM removal and filtered water quality is greater than the impacts of size. Floc size and strength appeared to be mostly related to the controlled parameter Fe:DOC.

It is possible that the method of quantifying the floc size by performing the jar test on the flocculated water contributed to the lack of correlation with the filtered water quality as the floc size was not measured directly going onto the filter. It is possible and likely that the floc size exiting the DA20 plant was not proportional to the floc size within the jar test, which would mean that the correlations between floc size and filtered water quality would not be valid or significant as has been shown.

Part 6.13 DA20 Pilot Plant Dosing Trial Conclusions

The main objective of the experimental work detailed in this chapter was as follows:

- Carry out pilot plant trials using the DA20 and pilot filtration column to evaluate the extent and relative importance of correlations between Fe:DOC ratio and floc properties, NOM removal and filter performance using a range of Fe:DOC above and below the literature reported optimum of 1.

Coagulant dose is commonly altered on treatment plants as a means to improve NOM removal performance or filter performance. It can be concluded that the following occurs both directly and indirectly when the Fe:DOC ratio is manipulated by increasing the ferric dose relative to the DOC:

- Floc size as measured by FI_{max} within the jar test increased, and as this increased the floc strength factor decreased. Floc reformation factor did not correlate strongly with any of the measured variables. FI_{max} was also found to be correlated with flocculated zeta potential, but not flotation zeta potential. Floc properties did not correlate significantly with NOM removal.
- NOM removal increased with Fe:DOC and was found to significantly relate to floted zeta potential, and there was evidence of the operational window for good removal as determined by Sharp *et al*. (2006). The range for good UV_{254} absorbance removal of <5 abs/m was found to be -9.6 mV to -2.7 mV within an overall range of -12.2 mV to -2.7 mV. Improvement was noted as the zeta potential approached 0 mV.
- Filter performance generally improved as measured by filtered particle counts and turbidity, with the most notable improvement observed in the particle count trends. The most significant correlation was found between floted zeta potential and filter effluent quality, with an improving trend noted as the zeta potential increased.
- Final end of run filter effluent quality was noted to deteriorate considerably within the lower bounds of the zeta potential range, and this was typified by breakthrough at low headloss when the zeta potential reached -12.2 mV.

The floc properties were assessed by means of the breakage jar test which was carried out on the DA20 flocculator inlet water. This method was adopted after preliminary tests using the PDA to measure the floc at the flocculator inlet, and flotation outlet failed to give stable readings. The method used was valid in terms of determining the impact of Fe:DOC ratio on floc properties and NOM removal, but conclusions relating to the impact of floc properties on filter performance were more subjective given that the shear stresses within the pilot plant were different to the jar. It was therefore difficult to say with certainty that the floc size in the jar was equivalent to the floc size entering the filter. The statistical analysis generated from correlation between FI_{max} and filtered particle counts showed that floc size was significantly related to the filter effluent quality, but was not a significant contributor when considering the inter-relationships as a whole. The correlation between the floc size in the flocculator and the floc size exiting the flotation units couldn't be quantified as the PDA reading was not stable enough at low turbidities, and so it was concluded that the relationship between floc properties and filter performance requires further investigation; particularly with the effects of changes in surface charge eliminated. This theme is continued in the experimental work in Chapter 7 where floc size will be increased without changing the zeta potential.

The effect of increased Fe:DOC on flocculated and floted zeta potential was found to increase as the relative coagulant dose increased and furthermore, the flocculated and floted zeta potential were found to correlate well with FI_{max}. The results showed that there was a significant decrease in zeta potential between the flocculators and the flotation outlet which implied that the flotation process affects the surface charge. The practical implication of this is that the coagulant dose should be tailored to the flotation outlet zeta potential to ensure good NOM removal, and not the flocculation zeta potential. Overall it is to be concluded that a Fe:DOC ratio of approximately 1.2 gave the best performance overall with respect to NOM removal, and stable filter effluent quality during summer conditions.

Chapter 7 The effect of polyelectrolyte dosing on floc properties and filter performance

Part 7.0 Introduction

The experimental work presented and discussed in Chapters 4 to 6 showed that coagulant dose relative to DOC content is a key parameter to optimise for NOM removal, with surface charge playing an important part in this relationship. As the Fe:DOC content increased so did the floc size, but the extent of floc breakage over the processes upstream of filtration is unknown but suspected to be quite large; particularly over the DAF process (Leppinen and Dalziel, 2004). The floc strength factor measured in the breakage jar test approximates the effect of imparting a high shear stress on the floc, and in general the floc strength factor decreased as the floc size increased. The work in Chapter 6 did not fully establish the extent of the link between floc properties and filter performance as the floc properties could not be measured at the exit of the flotation unit. The experimental work in this chapter addressed this by altering the floc properties closer to the filter inlet to model a closer approximation of the floc properties entering the filter during the pilot plant experiments. It was also important to be able to eliminate changes to surface charge, as previous experiments in Chapters 4 to 6 involved changes to both floc size and surface charge. In order to achieve this, both non-ionic and ionic flocculants were used; therefore any changes observed with non-ionic flocculants could be assumed to be due their flocculating effect rather than their surface charge effects.

In this experiment flocculants were dosed into pre-filtered water with the aim of identifying flocculants and dose ranges that increase floc size and strength. When suitable flocculants and dose range was established by means of jar tests, the pilot filtration trials were carried out to determine the effects of flocculant dose and type on filter performance. It is important to note that historically Albert WTW filters experience the problem of filtered turbidity breakthrough at low headloss during the winter months. This part of the work aimed to replicate this problem on the pilot filter, and to rectify it by altering the floc properties by dosing flocculant into the pre-filtered water.

Part 7.0.0 Breakage jar tests using Albert WTW DAF outlet water and flocculants at pH 6.5

Water was taken from Albert WTW DAF outlet channel with the aim of assessing re-flocculation characteristics of four types of flocculants over a low dose range of 0.002 mg/l-0.01 mg/l. The properties of the four flocculants are summarised below:

1. FL17 – cationic very high charge density liquid polymer. Charge is attributable to the polyamine group.
2. AH912 – very low charge density acrylamide homo-polymer formed by polymerisation of acrylamide monomer. Molecular weight very high and non-ionic.
3. AN905 – very low charge density polymer formed from co-polymerisation of acrylamide and sodium acrylate monomers. Very low charge density (anionic) and very high molecular weight.
4. FO4190 – low charge density polymer formed from the co-polymerisation of acrylamide and methyl chloride ADAM (trimethyl ammonium ethyl acrylate chloride). Very high molecular weight and cationic.

Floc carried over from the DAF process is suspected to be highly fragmented (Leppinen and Dalziel, 2004) and it was thought that small doses of flocculant could improve the filtration of the floc by improving its strength and size. This experiment was carried out in winter, and the temperature of the treated water was 7ºC on the full-scale plant and in the pilot plant area where the tests were carried out. The PDA was used to assess the dynamic flocculation performance using the flocculants on the treated water. The treated water was initially taken from downstream of the pre-filtered lime dosing where the pH was 6.5.

The experiments were carried out over 4 days when the full-scale plant was operating in a stable manner – coagulation pH was 4.5 and Ferripol XL dosing was consistent relative to the DOC content. As described in Chapter 3, each experiment was carried out three times for reproducibility. During the initial evaluation of the four flocculants there were no 0.45µm membrane filters onsite, and residual UV_{254} absorbance was not measured. This was rectified during the second set of jar tests taken from the pilot plant mixing tank.

Part 7.0.1 Albert WTW floted water quality during November 2004

Table 25 below shows the floted water quality of the 4 *15 litre bulk samples used over the experimentation period. This shows the water quality was stable in terms of surface charge but a little more variable in terms of turbidity, but reasonably comparable between the four flocculants. The raw water quality was stable over the four days (zeta potential -17.2 mV, SUVA 3.8 m-1 L/mg C, pH 6.4, turbidity 7.5 NTU) and the floted water quality shown in table 44 reflects this. The residual UV_{254} absorbance was approximately 5 abs/m which implies that the coagulant dosing was ok; but not ideal as achieving less than 5 abs/m was the Yorkshire Water target to reduce THM formation potential.

Sample No	Fe:DOC	Floted UV_{254} Absorbance (abs/m)	Floted Turbidity (NTU)	Coagulation zeta potential (mV)	Pre-filtered zeta potential (mV)	Polymer
1	1.5	5.1	2.8	-5.3	-10.8	FL17
2	1.5	5.0	3.6	-5.4	-10.7	AN905
3	1.5	5.1	2.6	-6.5	-11.2	AH912
4	1.5	5.2	2.5	-5.4	-11.3	FO4190

Table 44 Albert WTW water quality during 4 days of experiments in November 2003, 7°C. Coagulation pH 4.5 and pre-filtered pH 6.5.

Part 7.0.2 Dynamic flocculation curves using the PDA, Albert WTW floted water and flocculants

Figures 74 to 77 show the mean dynamic flocculation curves obtained from dosing each polymeric additive into the floted water using a dose range of 0.002 mg/l to 0.01 mg/l. The systems without additives always showed some re-flocculation, which was completely reversible. It was not possible to accurately fit the Sigmoid curve to the results as the r^2 coefficient of regression was <0.8 (figures obtained were in the range 0.7-0.77, with no fit using 0.01 mg/l), and so the dynamic flocculation parameters were determined from the flocculation curves. The flocculation curves generated using AN905, AH912 and FO4190 as shown in figures 74 to 76 all show a positive correlation between polymer dose and maximum floc size as measured by FI_{max}. The noise within the flocculation curves generally indicated that doses of above 0.008 mg/l were over-doses and couldn't be monitored effectively by the PDA. This was attributed to the flocculant nature of the additives used due to bridging of the polymer chains. This process eventually caused the floc to increase in size such that the number of floc particles passing through the PDA sensor reduced and the

reading became too noisy to correlate with floc size. This wasn't as problematic with AH912.

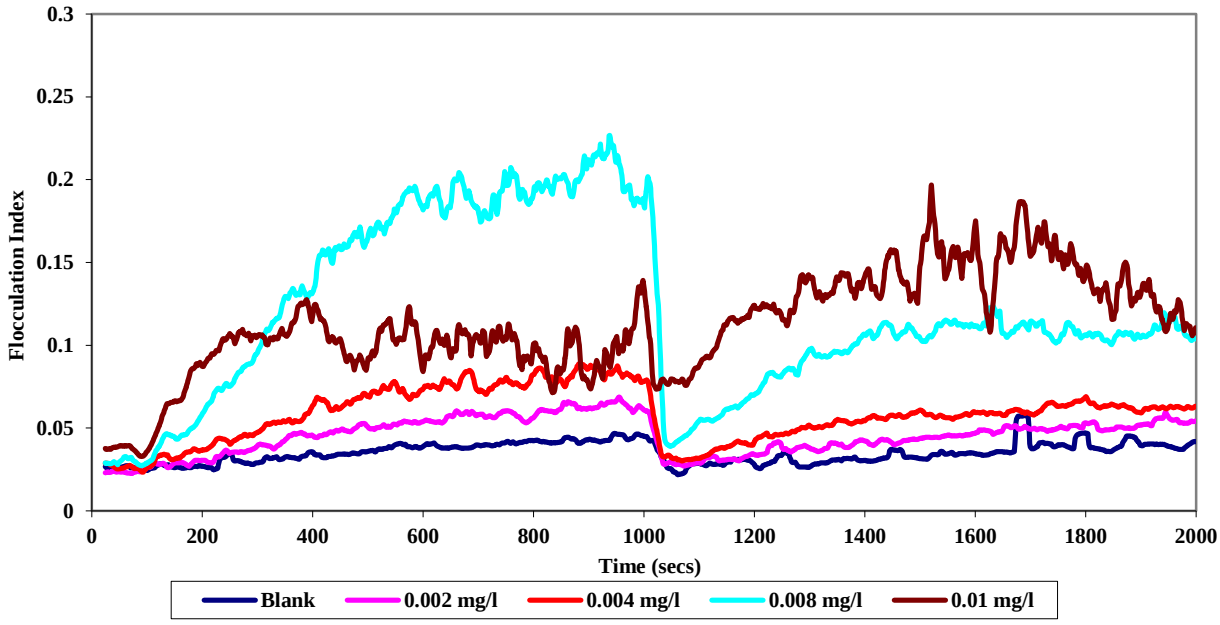


Figure 74 PDA flocculation curves using Albert WTW floted water at pH 6.5 and anionic flocculant AN905

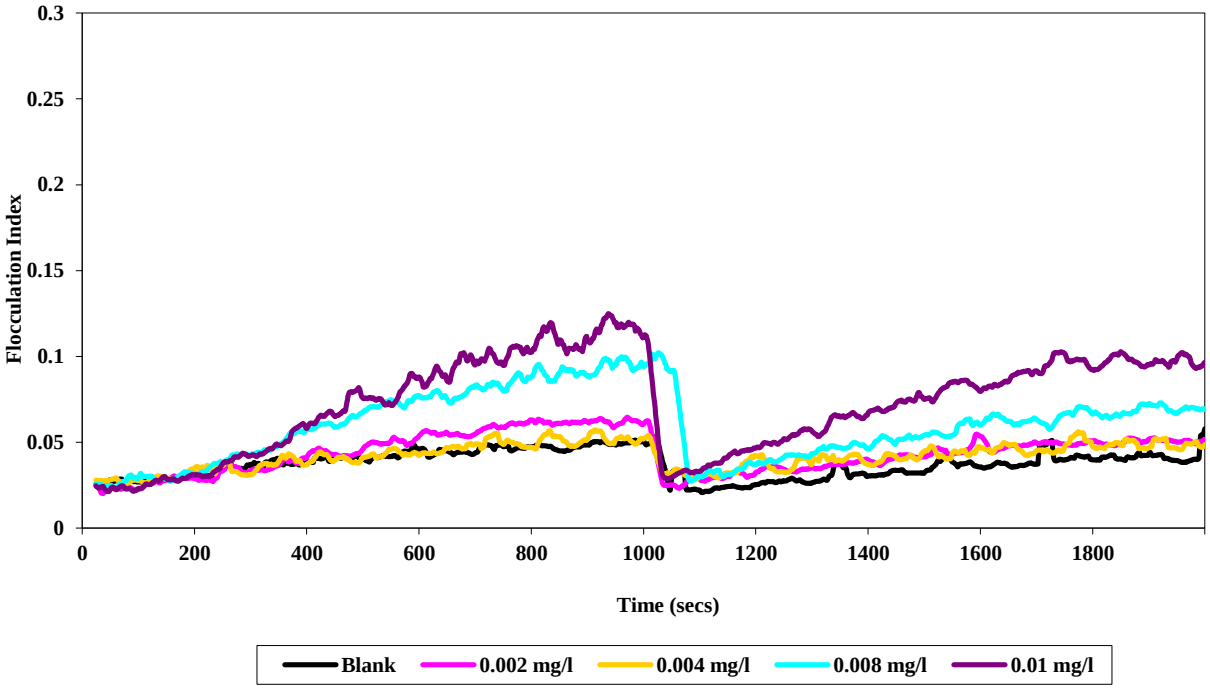


Figure 75 PDA flocculation curves using Albert WTW floted water at pH 6.5 and non-ionic flocculant AH912

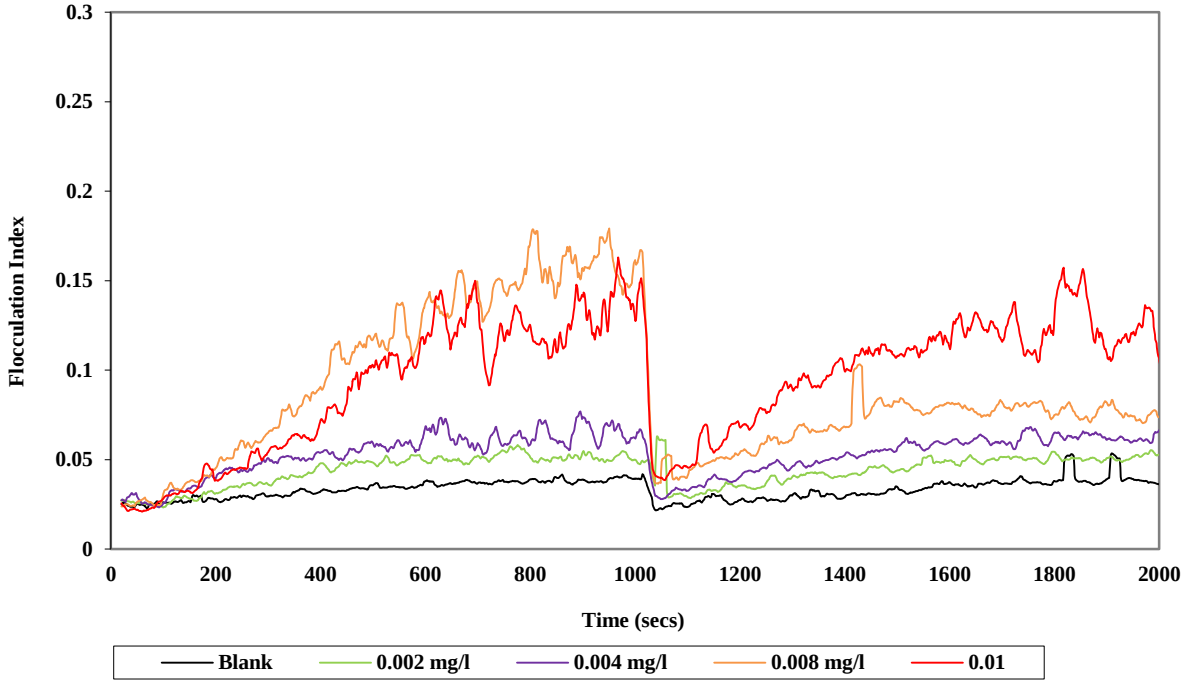


Figure 76 PDA flocculation curves using Albert WTW floted water at pH 6.5 and cationic flocculant FO4190

Figure 77 was generated using the high charge density cationic additive FL17, and this showed no effect on the floc size over the applied dose range. This was not surprising given that the raw water surface charge was reasonably well destabilised by the time that the water exited the flotation units. The coagulated water zeta potential during the four days of experiments was between -5.3 mV and -6.5 mV, which was within the operational window deemed to correspond to good performance. The additive FL17 exhibited no flocculating effect but a small increase in zeta potential was noted (see figure 82).

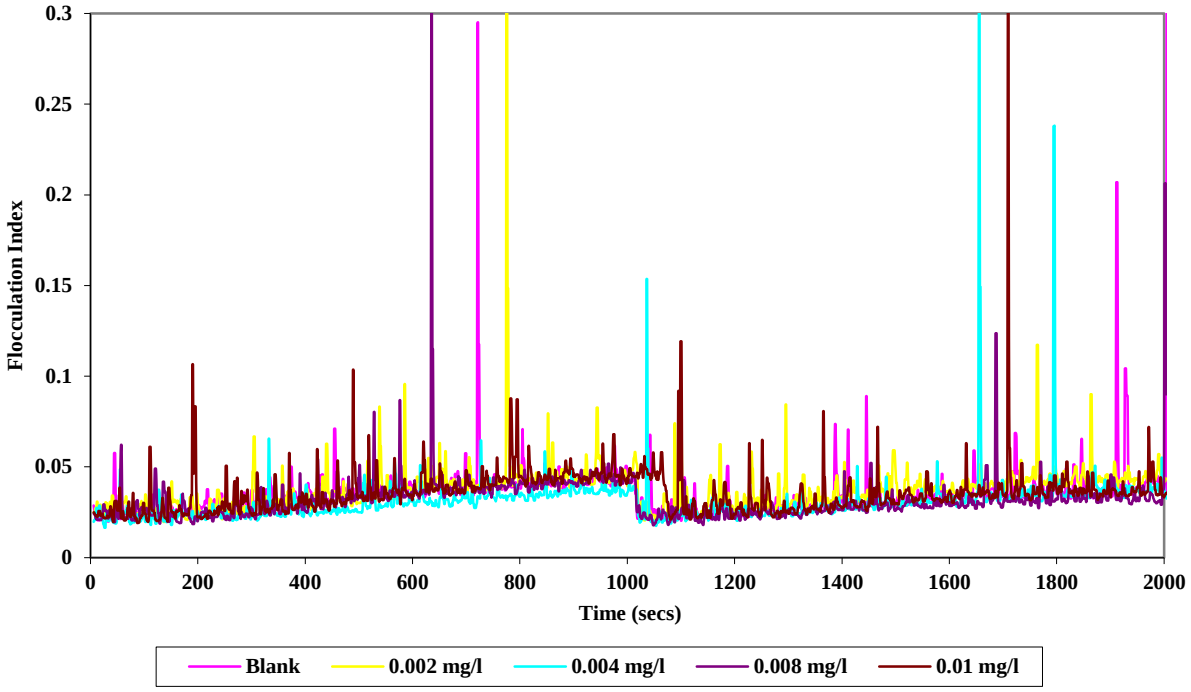


Figure 77 PDA flocculation curves using Albert WTW floted water at pH 6.5 and cationic additive FL17

Figure 79 shows the impact of the increased polymer dose on FI_{max} (interpreted from the curves rather than using Table Curve as regression coefficient was<0.8). The graphs all show a strong linear trend between flocculant dose and floc size as measured by FI_{max}. The non-ionic flocculant AH912 showed the smallest increase in FI_{max} followed by the cationic flocculant FO4190, and the largest increase was noted when using the anionic flocculant AN905. The slightly differing performance is most likely to have been due to the different functional groups and respective charges on the flocculants and how they interacted with the humic floc. All three were very high molecular weight compounds and were thought to act by polymer bridging between the chains. The superior performance of AN905 suggests that charge had an impact on the polymer action as all three were capable of polymer bridging. This implies that there was some positively charged floc that the anionic functional group adsorbed to that enabled more interaction and created larger floc. This difference in polymer performance is shown more clearly in figure 78 which compares the flocculation index curves generated using 0.008 mg/l of each of the flocculating polymers. This shows that not only was the flocculation relatively quicker using AN905 at a concentration of 0.008 mg/l but the extent of re-flocculation was also greater. This may have been due to the slightly higher floted water turbidity using AN905.

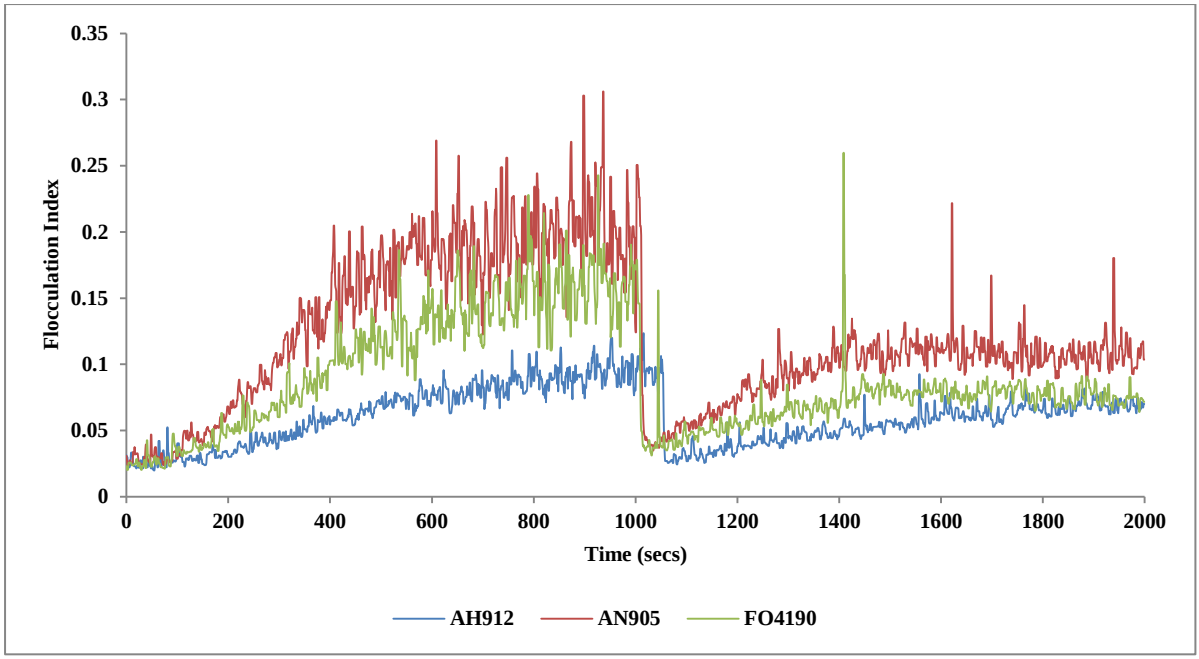


Figure 78 Comparison of flocculation index curves generated using 0.008 mg/l of AH912, AN905, FO4190 from breakage jar tests using Albert WTW floted water at 7°C and pH 6.5

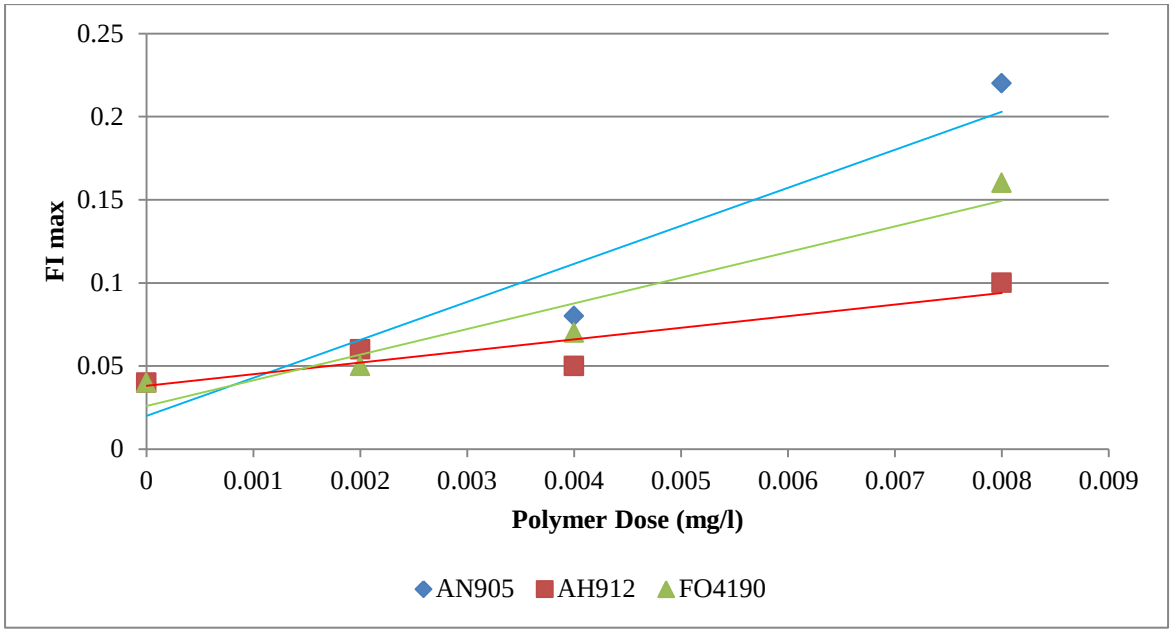


Figure 79 Impact of flocculant dose on FI_{max} determined from breakage jar tests using Albert WTW floted water at 7°C and pH 6.5

The derived parameters floc strength factor and floc reformation factor were calculated by using the data directly from the graphs. Figure 80 shows the effect of flocculant concentration on floc strength factor. The systems without flocculant addition showed the same degree of breakage. The floc strength factor showed a tendency to decrease relative to the blank systems without additives. This was consistent across the three flocculants.

The overall change in floc strength factor from the control systems with no additives to those dosed with 0.008 mg/l was around 50%. This implies that all three flocculants at a dose of 0.008 mg/l formed weaker floc (although larger) that was less resistant to the shear stresses imparted during the breakage part of the jar test when compared to the systems with no flocculant. The best results in terms of higher floc strength factor in the dosed systems were observed with the non-ionic flocculant AH912 at doses of 0.004 mg/l and 0.008 mg/l.

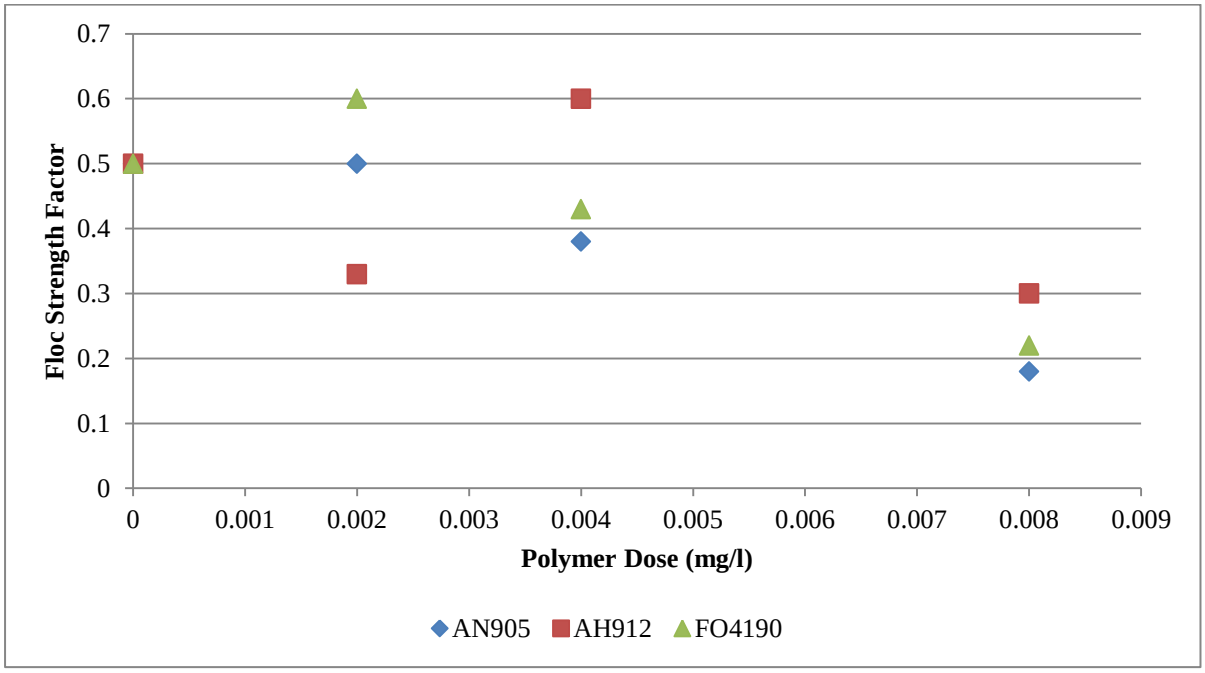


Figure 80 Impact of flocculant dose on floc strength factor determined from breakage jar tests using Albert WTW floted water at 7°C and pH 6.5

Figure 81 shows the impact of flocculant concentration on the floc reformation factor. The relationship was less clear than seen previously with the floc strength factor but showed a tendency towards decreased reformation factor as the concentration of flocculant increased from 0 to 0.008 mg/l. The systems with no additives showed complete floc reformation but the flocculant dosed systems did not exhibit the same performance. The flocculant dosed systems all exhibited a considerable decrease of approximately 50% in floc reformation over the concentration range applied. The systems with no additives all exhibited reversible re-flocculation by virtue of the jar test procedure. All flocculants expressed a linear relationship between dose and FI_{max}, and all flocculant doses above 0.004 mg/l gave rise to considerably larger floc that was comparatively weaker and less reversible than the re-flocculation observed with the control systems.

The non-ionic polymer showed the least deterioration in floc strength factor and floc reformation factor and also corresponded to the smallest system FI_{max}. This was highly likely to have been due to the relative size of the floc compared to the eddy size, the smaller floc formed with the non-ionic polymer was presumably smaller than the eddy size and therefore ruptured to a lesser degree.

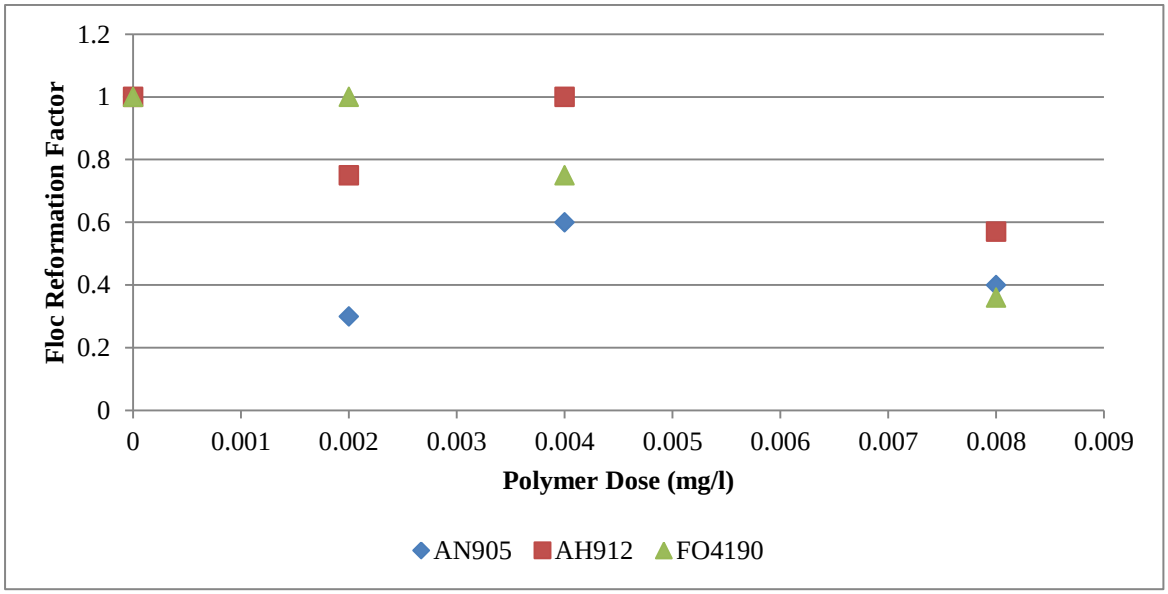


Figure 81 Impact of flocculant dose on floc reformation factor determined from breakage jar tests using Albert WTW floted water at 7°C and pH 6.5

Part 7.0.3 The effect of flocculant type and dose on zeta potential using Albert WTW floted water during November 2004

Figure 82 shows the effect of polymer concentration on the final settled zeta potential at the end of the jar tests. As would be expected, the non-ionic flocculant AH912 made no impact on the zeta potential. Work carried out by Fabrizi *et al*. (2010) using the same polymer on the same source water also reported no effect of dosing this flocculant on treated water zeta potential. The two cationic polyelectrolytes FO4190 and FL17 slightly increased the zeta potential but the effects were minimal. This was more noticeable with the very high charge density compound FL17 as would be expected. The anionic flocculant AN905 showed little impact on the zeta potential. Re-flocculation wasn't observed using FL17 but there was an appreciable change in zeta potential suggesting some adsorption of the polymer onto the humic floc but no polymer bridging. The flocculants were not expected to change the zeta potential appreciably as they were very low charge density compounds that were expected to flocculate via means of polymer bridging between the polymer chains.

The results in figure 82 were therefore to be expected, and provide a basis for altering physical floc properties without altering the surface charge.

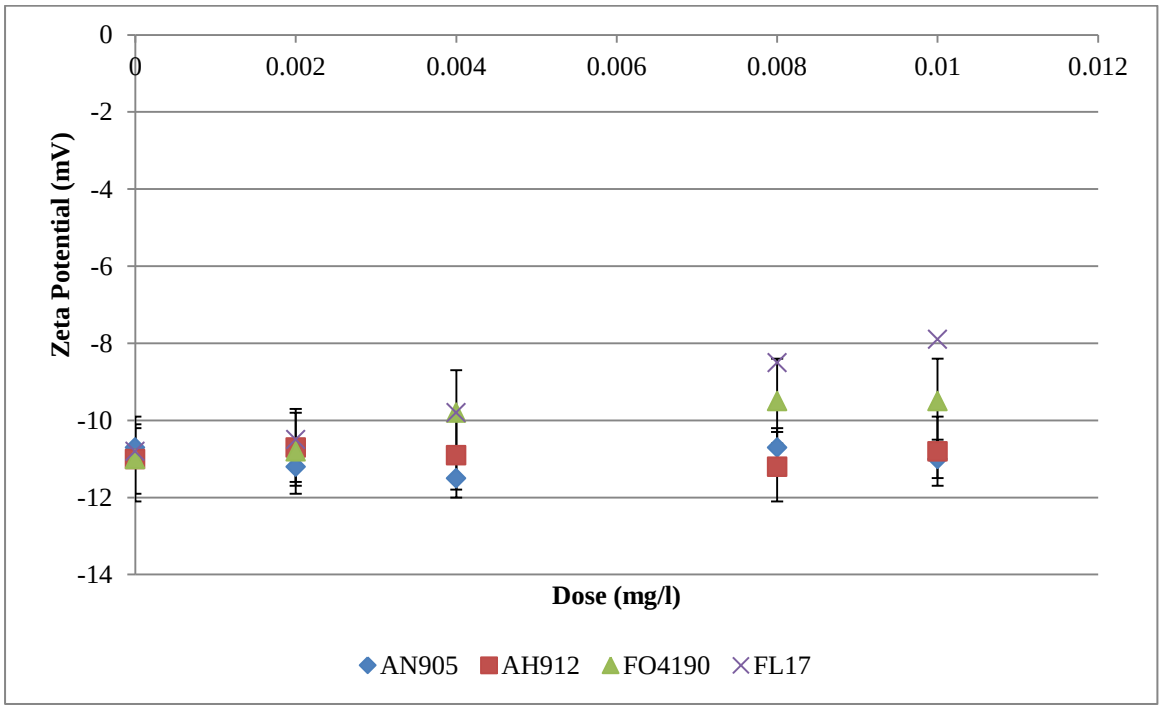


Figure 82 Flocculated zeta potential after jar tests using polyelectrolytes dosed into Albert WTW floted water at pH 6.5, November 2004 and 7°C

Part 7.0.4 Settled turbidity using AN905 at pH 6.5

The relationship between the concentration of the flocculating polymers AN905, AH912 and FO4190 and settled turbidity is indicated on figure 83. All the flocculants showed a strong correlation between dose and settled turbidity with a settled turbidity of <1 NTU achieved by the three flocculants using 0.01 mg/l. This reduction in turbidity is presumed to arise from the formation of denser more settleable floc by the addition of the polyelectrolyte. The floc dosed with FL17 showed no improvement in settled turbidity which corresponds with the dynamic flocculation curves showing no re-flocculation above the level seen with no additives. The largest reduction in settled turbidity over the applied dose range was observed using the anionic polymer AN905 which also corresponded to the system with the largest FI_{max}. At a dose of 0.01 mg/l all three flocculants exhibited good performance with settled turbidity of 0.6-1 NTU achieved. The settled turbidity was not affected by the dose of FL17 which was to be expected given the lack of flocculating ability already witnessed.

Overall the data shows that improvements in settled turbidity were observed with all three flocculants within the applied dose range. The PDA data showed however that doses of 0.01 mg/l formed large sticky floc which whilst settleable, may not be filterable without causing excessive headloss.

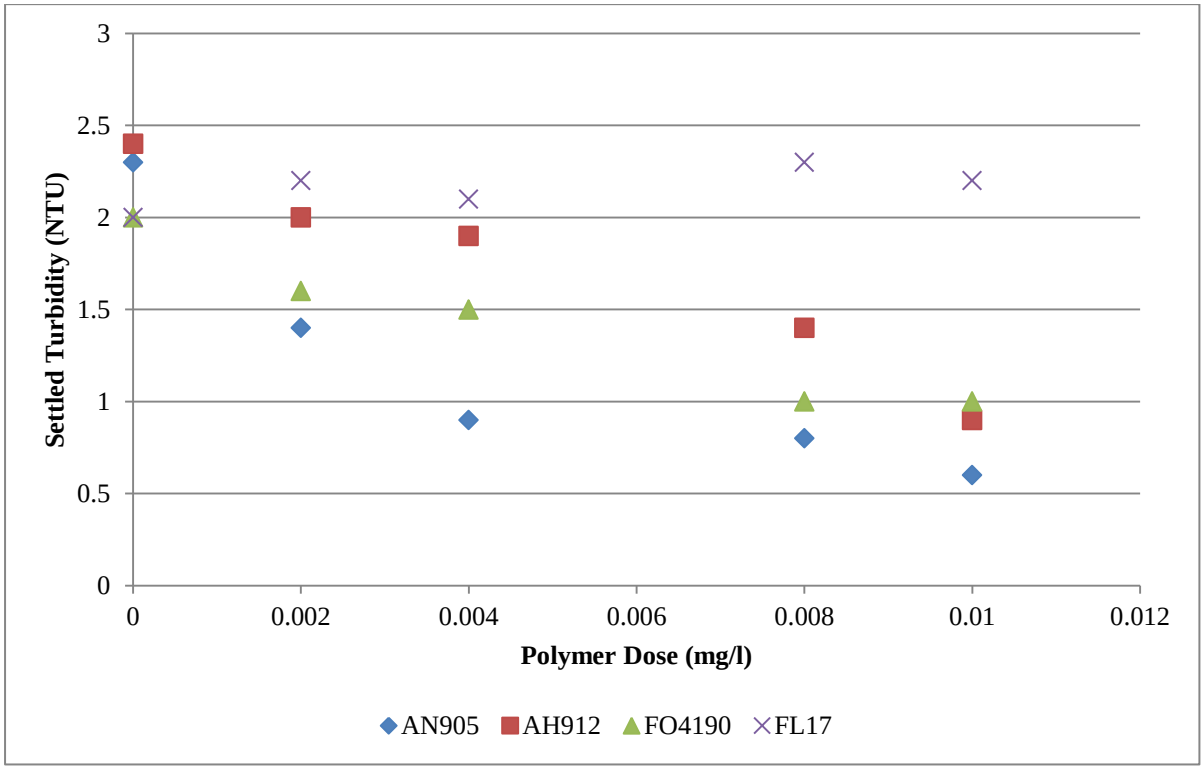


Figure 83 Settled turbidity after breakage jar tests using polyelectrolytes dosed into Albert WTW floted water at pH 6.5 (7°C) during November 2004

Part 7.1 Summary of Polymer Dosed Jar Tests using Albert WTW Floted Water at pH 6.5

The floted water quality was reasonably stable during the four days of experiments that the trials were carried out over. With the exception of the polyamine FL17 which showed no re-flocculation potential, there were some common results observed using the three flocculants AH912, AN905 and FO4190:

- The higher doses of 0.01 mg/l tended to produce large "sticky" floc that was difficult to obtain a good flocculation curve from. This was thought to be due to the number of flocs present in the jar being reduced significantly and as a result the PDA wasn't seeing a continuous stream of floc. The reading in these cases tended to be very noisy and exhibited saw-tooth features. This was more evident in the raw flocculation curves, rather than the curves shown in this chapter which have been smoothed by the "moving average" function to enable easy visual assessment. This sort of over-dose floc would not be beneficial on the treatment plant as polymer over-doses have been associated with filter mud-balls and surface clogging.
- Re-flocculation occurred in all systems without the use of additives, and generally this re-flocculation was completely reversible. Settled turbidity was seen to improve compared to the floted water by virtue of carrying out the jar test which was most likely due to the settlement period of 20 minutes at the end of the breakage test. On the treatment plant re-flocculation wouldn't be as extensive as in the jar tests as the water passes through a channel with baffles before entering the filters via a pill-box weir. It is therefore unlikely that significant re-flocculation could occur on the treatment plant between the flotation outlet and the filter inlet. The speed of re-flocculation is therefore an important factor in choosing the flocculant.
- Settled turbidity improved as the dose of polymer increased from 0.002- 0.01 mg/l - settled turbidity of <1NTU was achievable over this dose range.
- Zeta potential increased slightly with the use of the cationic additives FL17 and FO4190, but generally stabilised at 0.01 mg/l with no further increase. This suggests that the polymer has adsorbed to anions within the floc structure, and at doses above 0.01 mg/l these sites were full and the polymer was in excess. The same was true for the anionic additive AN905, but the non-ionic additive AH912 had no effect on the zeta potential as would be expected.

- The maximum flocculation index increased over the polymer dose range when using AH912, AN905 and FO4190, and this corresponded to a decrease in floc strength factor. Despite this, and as shown in figure 84 the flocculation index at the end of the breakage test (FI_{ref}) increased with increasing polymer dose. This shows that the flocs were larger at the end of the breakage test than the start, and the extent of the size increase was directly proportional to the polymer dose. This is important as it shows that even though the floc was subjected to considerable shear stresses during the rapid mix phase, the floc still re-formed and this reformation increased with polymer dose.

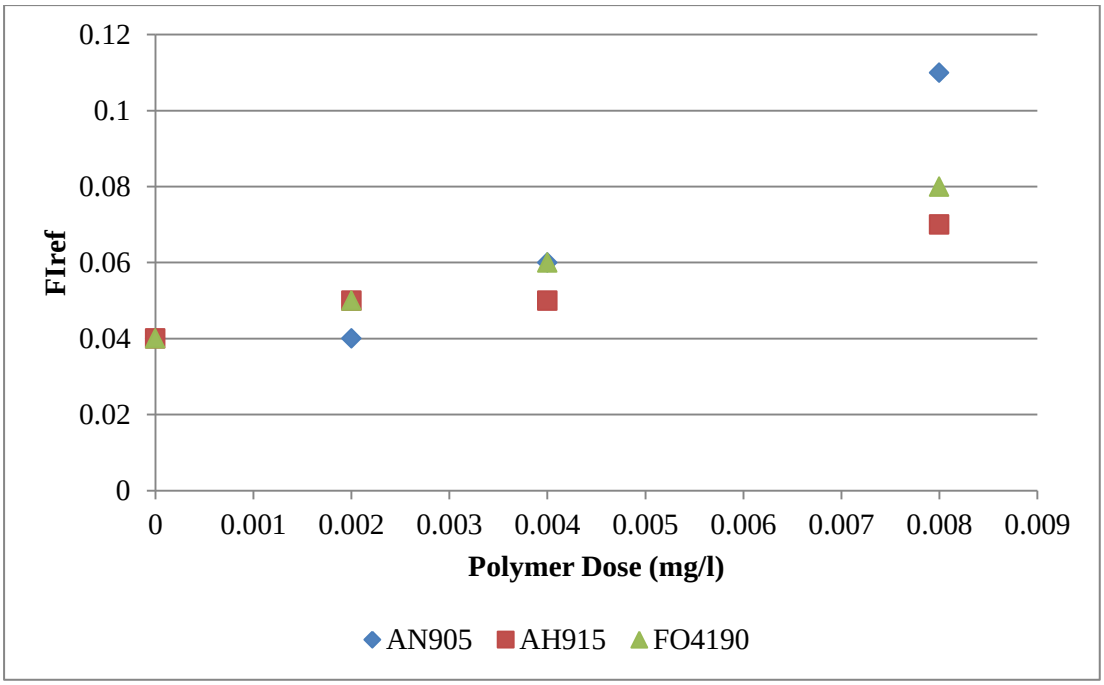


Figure 84 Flocculation index at the end of the breakage test (FI_{ref}) using AN905, AH912 and FO4190 and Albert WTW floted water at pH 6.5

- The PDA derived dynamic flocculation parameters floc strength factor and floc reformation factor were in general highest within the control systems with no additives.
- The flocculant dosed systems showed an overall increase in floc size throughout the tests, but with no enhancement of floc strength or reformation factors.

Table 26 shows a summary of the jar test performance sorted with respect to the best settled turbidity. Overall the performance of FL17 and FO4190 was inferior to AH912 and AN905, and was not investigated further. The next stage in the trial involved dosing the chosen polymers into the pilot filter plant mixing tank. The initial breakage jar tests summarised below have facilitated relatively easy identification of suitable polymers and dose ranges, but it is recognised that the pilot plant dosing trials require further optimisation of the dose.

Polymer	Properties	Dose (mg/l)	Mean Floted Turbidity (NTU)	Mean Dosed Turbidity (NTU)	Mean Floted Zeta Potential (mV)	Mean Dosed Zeta Potential (mV)
AN905	Anionic, low charge density	0.01	3.6	0.6	-10.7	-11
AN905	Anionic, low charge density	0.008	3.6	0.8	-10.7	-12.5
AH912	Non-ionic, low charge density	0.04	2.6	0.8	-11	-11.8
AN905	Anionic, low charge density	0.004	3.6	0.9	-10.7	-11.5
AH912	Non-ionic, low charge density	0.01	2.6	0.9	-11	-10.8
FO4190	Cationic, low charge density	0.01	2.5	1.0	-11	-9.4
AN905	Anionic, low charge density	0.04	3.6	1.0	-10.7	-10.9
FO4190	Cationic, low charge density	0.008	2.5	1.0	-11	-9.5
AN905	Anionic, low charge density	0.002	3.6	1.4	-10.7	-11.2
AH912	Non-ionic, low charge density	0.008	2.6	1.4	-11	-11.2
FO4190	Cationic, low charge density	0.004	2.5	1.5	-11	-9.8
FL17	Cationic, high charge density	0.04	2.81	1.5	-10.8	-7.4
FO4190	Cationic, low charge density	0.002	2.5	1.6	-11	-10.8
FO4190	Cationic, low charge density	0.04	2.5	1.7	-11	-10.5
FL17	Cationic, high charge density	0.008	2.81	1.7	-10.8	-8.5
FL17	Cationic, high charge density	0.004	2.81	1.8	-10.8	-9.8
FL17	Cationic, high charge density	0.01	2.81	1.9	-10.8	-7.9
AH912	Non-ionic, low charge density	0.004	2.6	1.9	-11	-10.9
AH912	Non-ionic, low charge density	0.002	2.6	2.0	-11	-10.7
FL17	Cationic, high charge density	0.002	2.81	2.1	-10.8	-10.5

Table 45 Summary of breakage jar test water quality results using four polyelectrolytes dosed into Albert WTW floted water at pH 6.5 and 7ºC during November 2004

Part 7.2 Effects of flocculant dosing on floc properties and pilot filter performance

Part 7.2.0 Introduction

The pilot filter plant illustrated in chapter 3 and used in the DA20 filtration trials was used to assess the effect of polymer dosing on filter performance. The experimental methodology is also described in Chapter 3. The breakage jar tests were carried out using water taken directly from the pilot plant mixing tank in order to derive the floc strength and reformation factors which have been used as performance monitoring parameters throughout this work. The following parameters were monitored during the filtration trials:

- UV_{254} absorbance and DOC (hourly readings during the filter run)
- Turbidity, particle counts, headloss and flowrate (online measurements)
- Zeta potential (hourly readings during the day)
- Dynamic flocculation performance (3 breakage jar tests per filter run taken from the pilot plant mixing tank located above the pilot filter inlet)

Initial tests using the doses indicated by the previous set of jar tests on the pilot plant didn't result in appreciable re-flocculation, and a new dose range of 0.005-0.05 mg/l was established. There could have been many reasons for the dose range not being equivalent between the jar tests and the pilot plant:

- The pilot plant feed point was moved to upstream of the pre-filtered lime addition as the lime dosing plant suffered from frequent failures which could have impacted on the pilot plant trial.
- Mixing conditions in the jar test were not identical to those in the mixing tank on the pilot plant as tank dimensions and stirrers were not the same.

The change in pilot plant feed point was necessitated by a series of secondary lime dosing failures on the main plant and was not thought to have an effect on the polymer action, as figure 85 shows.

The results in figure 85 were generated from a set of jar tests carried out on floted water upstream and downstream of the lime addition point to verify that there was no change in performance due to the pH decrease from 6.5 to 4.5. The results were comparable at both pH conditions and showed very similar performance to the jar tests results.

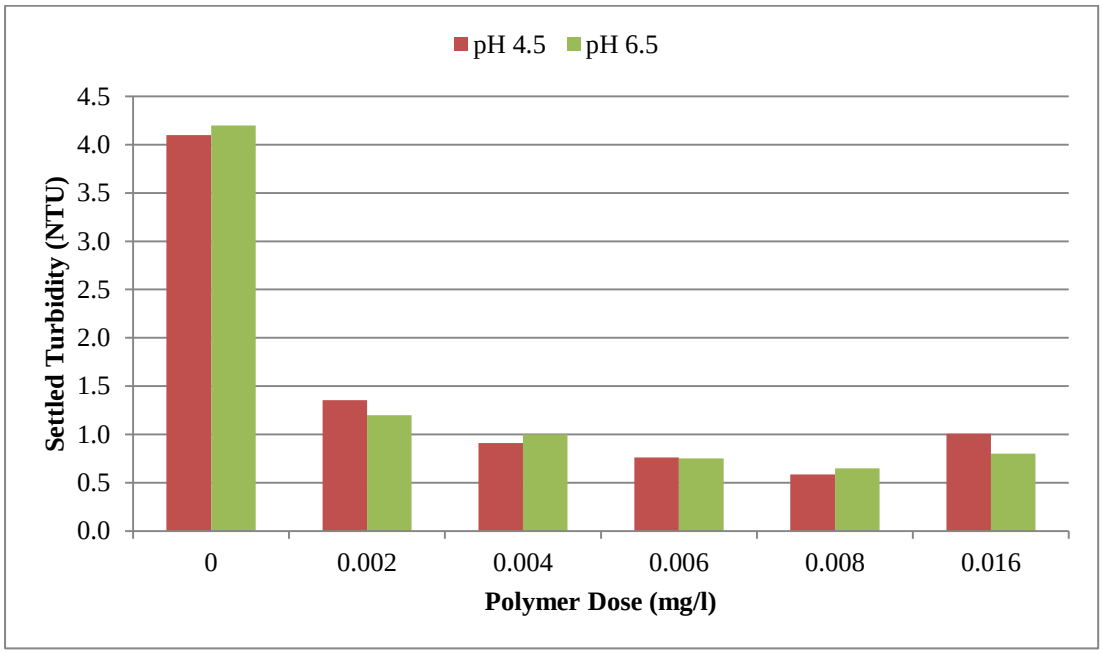


Figure 85 Effect of pH on settled water turbidity using AN905 dosed into Albert WTW floted water pre and post lime dose, 7 °C December 2004

Part 7.2.1 Influent water quality November - December 2004 at Albert WTW during pilot plant polymer dosing trial using AH912 and AN905

Table 27 shows the mean water quality upstream of the pilot plant during each filter run for both polymers. Each individual run took a day to complete and the experiments with the two polymers were carried out on consecutive weeks in November/December 2004. The non-ionic polymer AH912 was trialled first. The data shows that there was more variability during this experiment than earlier work which is to be expected as the pilot plant was fed directly from the main plant and was subjected to the variability of the raw water treatment process rather than when using bulk samples of the same water. Overall the 2nd week of experiments using AN905 were subjected to raw water of a higher humic substance concentration as measured by DOC and UV_{254} absorbance, but a lower floted turbidity. Despite this difference in raw water DOC, UV_{254} absorbance and Fe/DOC ratio the floted water zeta potential was comparable between the two polymer trials.

The floted water zeta potential was just outside of the upper end of the range derived by Sharp *et al.* (2003) of -10 to +3 mV thereby suggesting an overdose of coagulant on the main plant. The floted water UV_{254} absorbance was significantly higher during the 1st trial using AH912, but the floted water DOC levels were comparable between the 2 trials. Overall this suggests that the upstream treatment at Albert WTW wasn't performing optimally during the first polymer dosed pilot filter trial using AH912 in terms of floted turbidity and UV_{254} absorbance but by the second trial, both of these parameters had improved considerably. The reasons for the discrepancy between the floted water DOC and UV_{254} absorbance results were not known exactly but could be due to the accuracy of the different techniques.

Polymer	Dose (mg/l)	Raw water DOC (mg/l)	Raw water UV_{254} Absorbance (abs/m)	Fe/DOC	Ferripol XL dose (mg/l as Fe3+)	Floted water Zeta Potential (mV)	Floted water Turbidity (NTU)	Floted Water DOC (mg/l)	Floted Water UV_{254} absorbance (abs/m)
AH912	0	9	37	1.7	15	4	4.5	2.3	7.9
AH912	0.005	9	37	1.7	15	4.1	4.5	2.3	7.9
AH912	0.01	9.2	37	1.6	15	3.9	4.5	2.4	8.3
AH912	0.02	9.5	37	1.6	15	3.4	3.8	2.3	8.2
AH912	0.05	8.6	34	1.7	15	3.8	4.1	2.3	3
AN905	0	10.5	35	1.3	13.5	3.8	2.7	2.6	3.4
AN905	0.005	10.6	35	1.3	13.5	3.9	2.7	2.5	3.3
AN905	0.01	10.6	34	1.3	13.5	3.8	2.6	2.3	3.5
AN905	0.02	10.6	34	1.3	14	4.1	3.4	2.1	3.9
AN905	0.05	10.6	34	1.3	14	3.9	3.4	2.3	2.9

Table 46 Mean water quality upstream of the pilot plant at Albert WTW, November-December 2004, 7 °C.

Part 7.2.2 Dynamic flocculation curves generated from the pilot plant mixing tank at pH 4.5 using AH912 and AN905

Figure 86 shows that in the control sample tests with no additives, re-flocculation occurred as was observed in the earlier polymer dosed jar tests in this chapter and floc reformation was good. The PDA derived flocculation curves were much more distinct during the first polymer trial using AH912 and the dynamic flocculation parameters could be derived with reasonable confidence. The general trend showed increased floc index as the polymer dose increased, with a more marked increase at the highest dose. The data set from the second trial proved too noisy to interpret as shown in figure 87 and the dynamic flocculation parameters weren't derived.

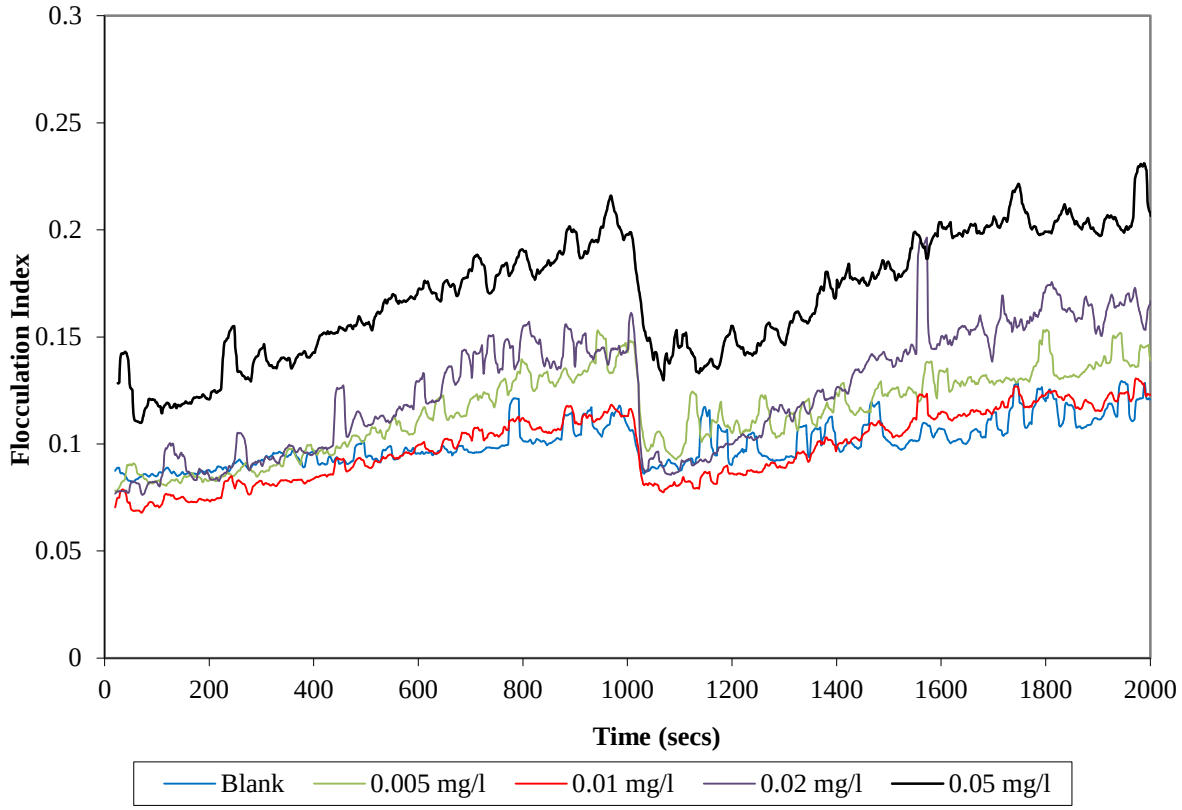


Figure 86 Dynamic flocculation curves using AH912 (0-0.05 mg/l) and water from the pilot filter plant mixing tank at Albert WTW in November- December 2004, 7°C

The flocculation curves shown in figure 87 were too noisy to be interpreted adequately by the curve-fitting software, or graphically and as a result the dynamic flocculation data wasn't used to calculate the floc reformation and strength factors. The flotation outlet turbidity was lower than the previous trial using AH912 which may explain the poorer quality flocculation curves. This suggests that there is a minimum turbidity; below which the PDA output is difficult to analyse with confidence. The flocculation curves obtained previously in the jar tests using the flotation outlet water showed clearer flocculation curves and the re-flocculation was more visible than shown in figure 87. The mixing conditions were the same between the two trials using AH912 and AN905, and the only difference thought to contribute to the poorly defined flocculation curves was the turbidity which was lower in this experiment using AN905 than the trial using AH912.

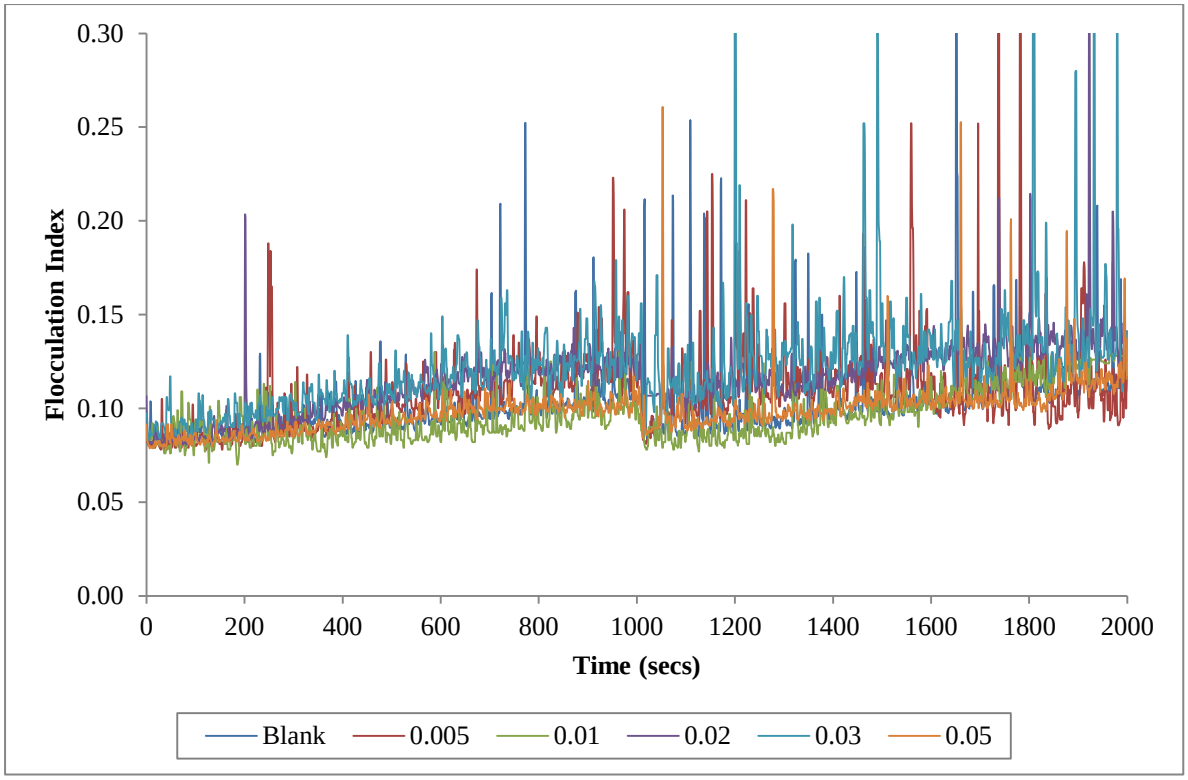


Figure 87 Dynamic flocculation curves using AN905 (0-0.05 mg/l) and water from the pilot filter plant mixing tank at Albert WTW in November-December 2004, 7°C

The data shown below in figure 88 which was derived graphically from figure 88 showed that FI_{max} exhibited a proportional relationship with polymer dose as seen previously. Floc strength factor decreased as FI_{max} increased as has been seen throughout this work, and FI_{ref} and FI_{max} were in essence equivalent, as the floc reformation factor was very high in all cases and showed complete reversibility by the end of the jar test.

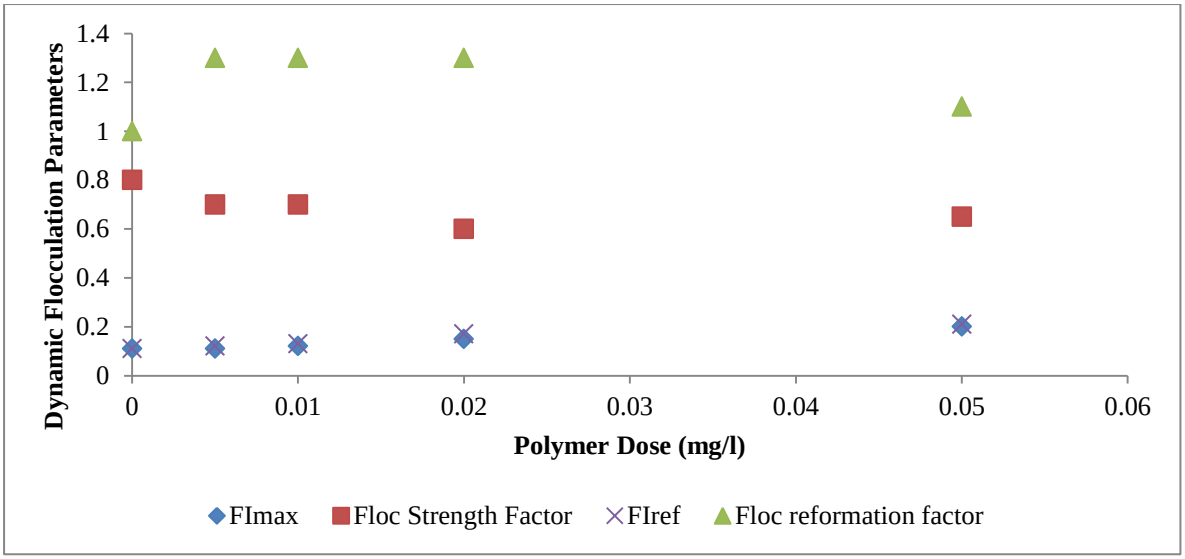


Figure 88 Dynamic flocculation parameters using AH912 (0-0.05 mg/l) and water from the pilot filter plant mixing tank at Albert WTW in December 2004, 7°C and pH 4.5

Part 7.2.3 Effect of dosing AH912 and AN905 on pilot plant mixing tank zeta potential

Figure 89 shows that as seen previously, the effect of the non-ionic flocculant AH912 on the zeta potential within the pilot plant mixing tank was negligible. The mildly anionic flocculant AN905 had no impact on the zeta potential until the dose reached the highest dose of 0.05 mg/l whereupon there was a slight decrease observed. The actual change between the floted and dosed zeta potential at 0.05 mg/l using AN905 was only 1 mV which is not a strong result. Zeta potential is therefore not thought to be a variable in these experiments. These results agree with those noted earlier in the preliminary jar tests in this chapter.

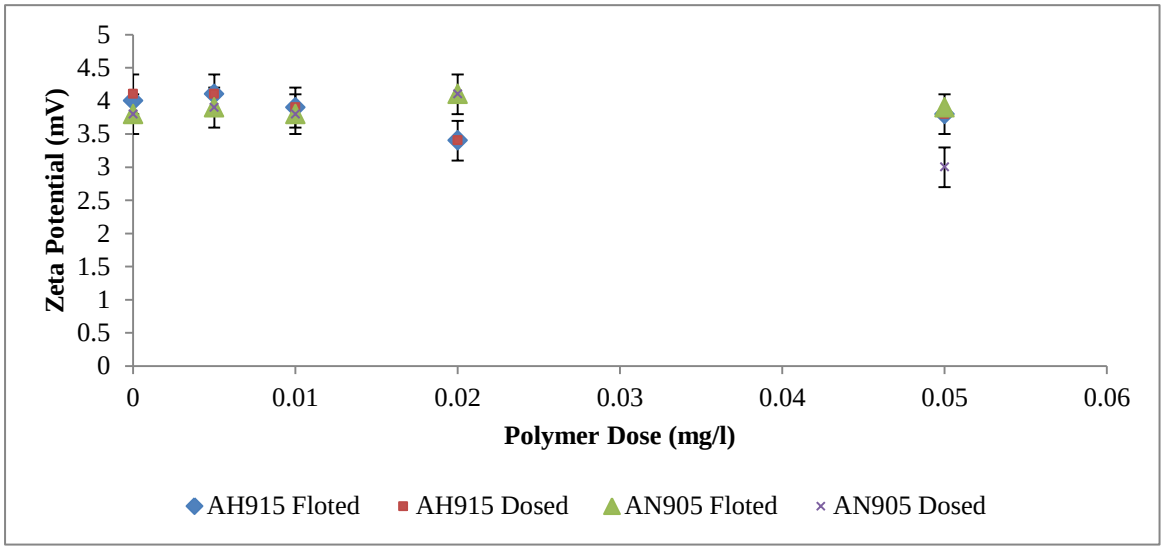


Figure 89 Zeta Potential Floted water dosed with AH912 from Pilot Plant Mixing Tank using AH912 (0-0.05 mg/l) and water from the pilot filter plant mixing tank at Albert WTW in November 2004, 7°C and pH 4.5

Part 7.2.4 NOM removal using AH912 and AN905

It was not known from the initial jar tests detailed in part 7.0 whether the flocculants used had any beneficial effect on the removal of residual humic substances as these parameters weren't measured due to a lack of membrane filters. These parameters were analysed for during the pilot filter experiments and the results are shown in figure 90. Figure 90 showed an increased removal of humic substances as either polymer dose increased to 0.05 mg/l but very little change was noted from the base level at the lower doses. The effect was more notable as measured by UV_{254} absorbance but both parameters followed the same pattern. The removal was calculated between the floted water and the filter outlet.

It was also evident that there was a small degree of UV_{254} absorbance removal over the pilot filter without additives. The mean water quality parameters measured during each run are shown in table 47. The most significant removal was achieved using either flocculant at a dose of 0.05 mg/l, and both polymers removed a similar proportion of either DOC or UV_{254} absorbing compounds. Influent water SUVA was noted to decrease from 3.6 to 1.3 m-1 L/mg C as the dose of AH912 increased from 0.02 to 0.05 mg/l, and this coincided with a decrease in raw water UV_{254} absorbance from 37 to 35 abs/m (DOC from 9.5 to 8.6 mg/l). This implies that there may have been a change in the balance of hydrophobic material in the raw water and consequently the pilot plant feed water. Lower SUVA values of <3 m-1 L/mg C indicate that the material is mainly hydrophilic (Edzwald and Tobiason, 1999), and these are usually reported to be the most challenging to remove via conventional coagulation (Parsons *et al.*, 2004). This did not appear to impact on the extent of UV_{254} absorbance removal or DOC removal associated with the polymer dose. It is possible that the polyelectrolytes targeted the hydrophilic compounds at the dose of 0.05 mg/l.

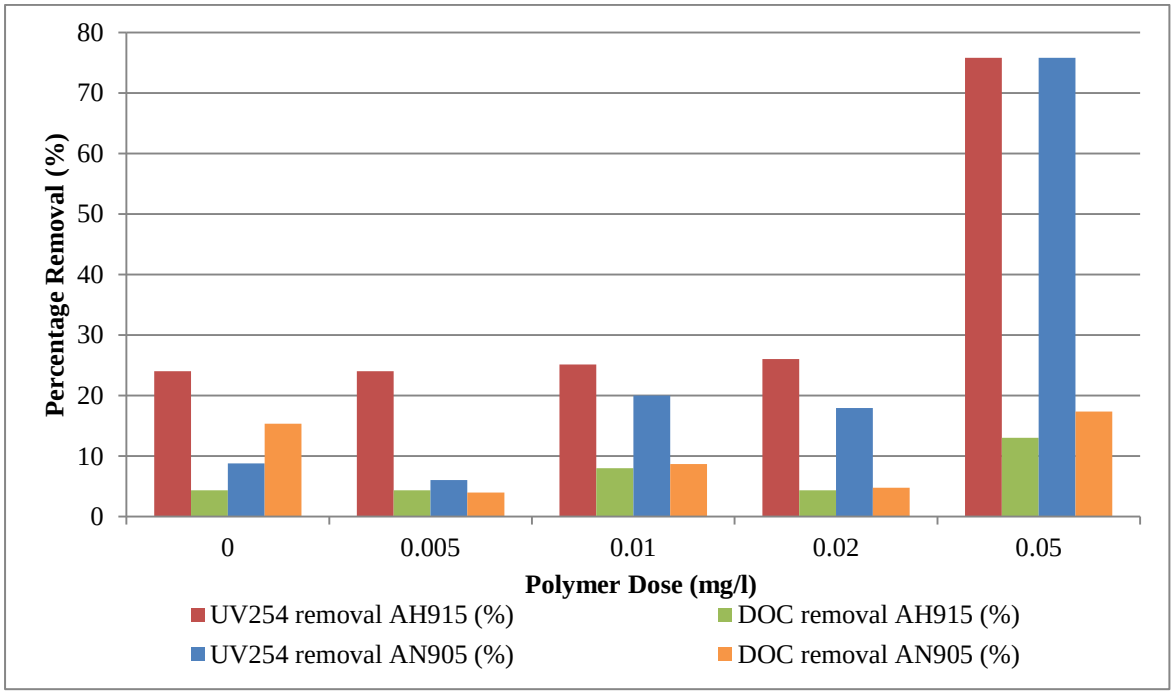


Figure 90 Removal of UV_{254} absorbance and DOC between flotation outlet and pilot filter outlet using flocculants AH912 and AN905, pH 4.5, 7 °C, November 2004

Polymer	Dose (mg/l)	Floted water SUVA (m-1 L/mg C)	Floted Water UV_{254} absorbance (abs/m)	Floted Water DOC (mg/l)	Mixing Tank UV_{254} absorbance (abs/m)	Mixing tank DOC (mg/l)	Pilot filter UV_{254} absorbance (abs/m)	Pilot Filter DOC (mg/l)	Filtered water SUVA (m -1 L/mg C)
AH912	0	3.4	7.9	2.3	6.5	2.3	6	2.2	2.7
AH912	0.005	3.4	7.9	2.3	6.5	2.2	6	2.2	2.7
AH912	0.01	3.4	8.4	2.5	6.3	2.5	6.3	2.3	2.7
AH912	0.02	3.6	8.3	2.3	6.9	2.5	6.1	2.2	2.8
AH912	0.05	1.3	3	2.3	0.9	2	0.7	2	0.4
AN905	0	1.3	3.4	2.6	3.4	2.1	3.1	2.2	1.4
AN905	0.005	1.3	3.3	2.5	3.2	2.1	3.1	2.4	1.3
AN905	0.01	1.5	3.5	2.3	3.2	2	2.8	2.1	1.3
AN905	0.02	1.9	3.9	2.1	3.9	2	3.2	2	1.6
AN905	0.05	1.3	2.9	2.3	0.9	2.3	0.7	1.9	0.4

Table 47 Mean water quality measurements during pilot filter trials using flocculants AH912 and AN905, pH 4.5, 7 °C, November 2004

Part 7.3 Pilot Filter Performance using AH912

Figure 91 shows the effect of increasing AH912 dose on filter effluent particle counts in the size range 2-5µm. Filter breakthrough was apparent in all runs, with the exception of the highest dose of 0.05 mg/l. Filter breakthrough was delayed as the dose increased, and the baseline quality similarly improved. The most successful dose appeared to be 0.05 mg/l which was the only run to maintain a good baseline particle count without breakthrough. As mentioned in Chapter 3, the online data from the control filter runs carried out at the start of each filter trial was lost due to a corrupted disk and therefore aren't included in the analysis.

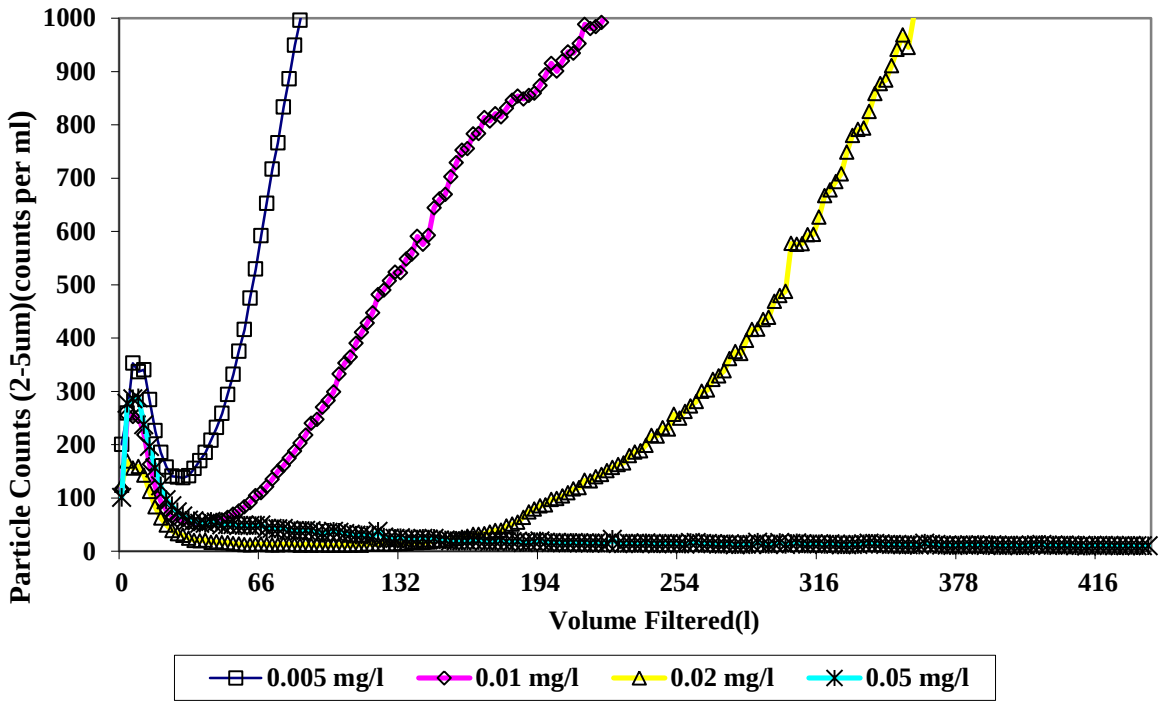


Figure 91 Filtered particle Counts using AH912, pH 4.5, 7°C, November-December 2004

Figure 92 shows that turbidity exhibited the same breakthrough pattern as seen with the particle count measurements. The first two runs using 0.005 mg/l and 0.01 mg/l showed particularly poor performance with breakthrough occurring very early into the run. The final two runs showed a better performance with a baseline of good water quality and no breakthrough using 0.05 mg/l. The ripening peak using 0.05 mg/l and 0.01 mg/l showed an initial spike at the start which wasn't captured on the particle counter due to a slight delay in recording the data. The initial spike could have been due to backwash remnants, or particulate already present in the turbidimeter that wasn't flushed clear from previous run.

Both initial spikes were very short-lived and due to the early stage in the run would not have come from the influent water as the residence time was too short. The start of the ripening peak due to the influent water given a flowrate 5.5 m/h should be at approximately 25 mins or 33 litres filtered. Both of the early spikes in turbidity occurred at <33 litres so would not have originated from the influent water. The reasoning for plotting filtered water quality versus volume of water filtered rather than time was to account for any errors in the manual setting of the filter outlet valve and to allow for different hydraulics due to headlosses. This enabled comparison of the filter runs normalised to the volume filtered.

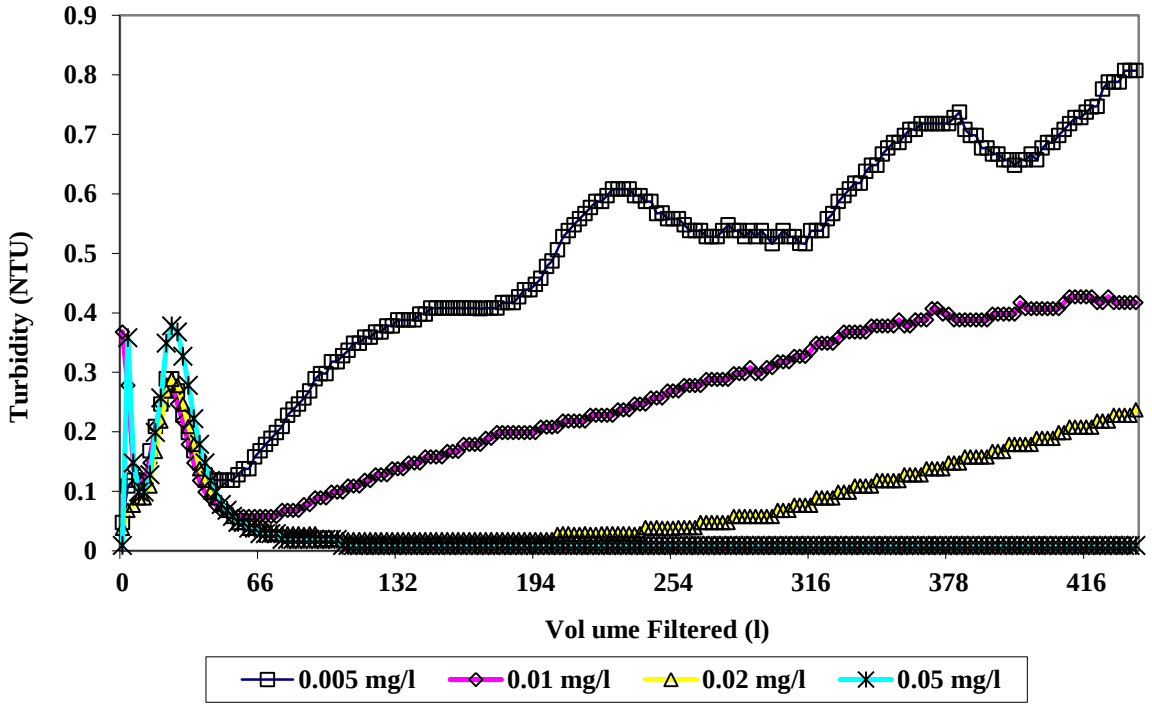


Figure 92 Filtered turbidity using AH912 pH 4.5, 7°C, November 2004

Part 7.4 Flow change experiments using the pilot filter plant and AH912

The flow change experiments were designed to test the resilience of the filter deposit to changes in the hydraulic shear forces, as flow changes have been well documented to cause filter breakthrough (Fitzpatrick *et al*., 1999). The assumption in this case was that the polymer dosed floc may prove more resilient to the flow changes which would further enhance the case for dosing polymer prior to filtration as a filtration aid.

The pilot filter results using the non-ionic polymer AH912 showed good performance using 0.05 mg/l with low filtered turbidity and particle counts and more importantly, no breakthrough and therefore less risk of passage of Cryptosporidium oocysts. This dose was then used in the following flow change experiments. The pilot filter was subjected to a 50% flow change of 1 hour duration at 3 hours and 6 hours into the run, with the objective being to see how the filter responded to the flow change with respect to effluent particle counts and turbidity. These experiments were carried out during a period of stable water quality on the full-scale plant, and were carried out directly after the pilot plant filter dosing trial detailed in part 7.2.5. The only difference in influent water quality was a decrease in turbidity from approximately 4 NTU to 2.5 NTU. The flow changes at 6 hours were thought to be representative of "shocking" a full bed depth filter at the end of its run when it is known to cause the most particle shedding according to (Fitzpatrick *et al*., 1999). This was based on 12 hour run times at Albert WTW during this period on 0.9 m bed depths. The pilot filter was half the bed depth and therefore thought to be equivalentally loaded in half the time.

Part 7.4.0 50% Flow change at 3 hours using 0.05 mg/l AH912 at pH 4.5 and 7ºC

The flow increment of 50% was initiated 3 hours into the filter run, and figure 93 shows the filter performance alongside the inlet turbidity from the flotation outlet. Figures 93 and 94 show that as seen before in Chapter 6, the periodic de-sludging of the flotation units gave rise to sharp increases in flotation outlet turbidity. These spikes in turbidity did not seem to affect the filter performance. The flow change did not cause breakthrough in either turbidity or particle count measurements. The data from the repeat run depicted in figure 94 showed a very similar performance, floted water turbidity was slightly higher in the second run but both filtered turbidity and particle counts exhibited a stable baseline despite the flow change. Filtered turbidity and particle counts again showed no breakthrough throughout the run, and no visible effect of the flow change.

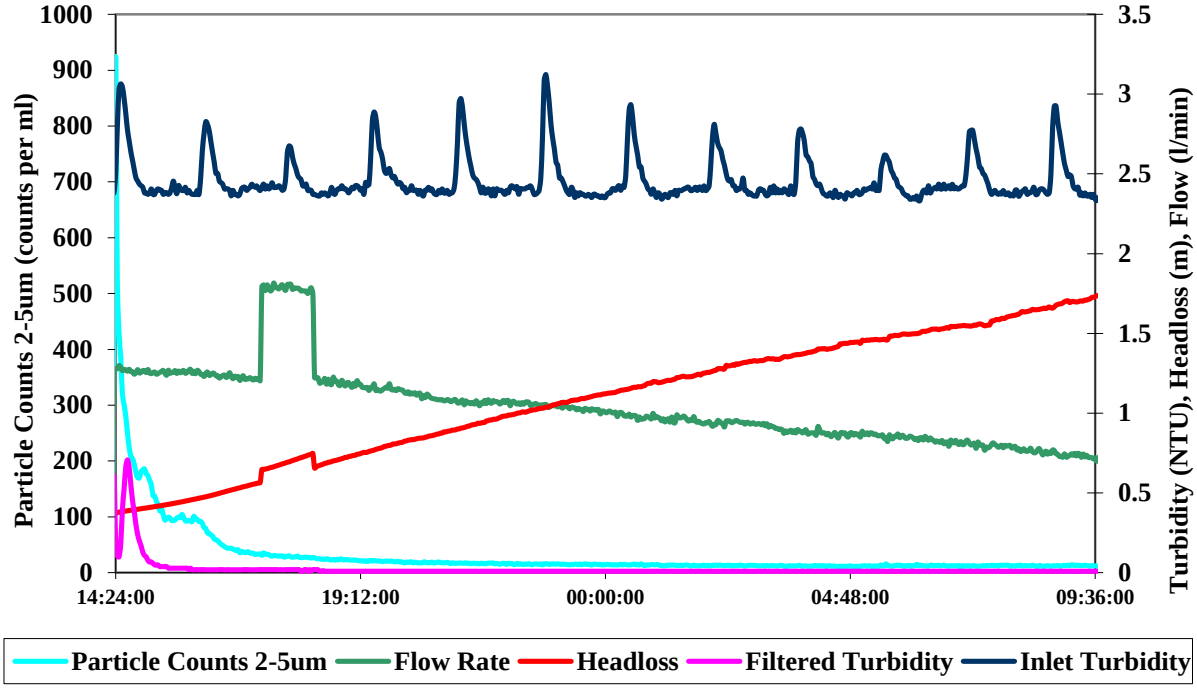


Figure 93 50% Flow change at 3 hours using 0.05 mg/l AH912 Run 1 pH 4.5, 7°C, November 2004

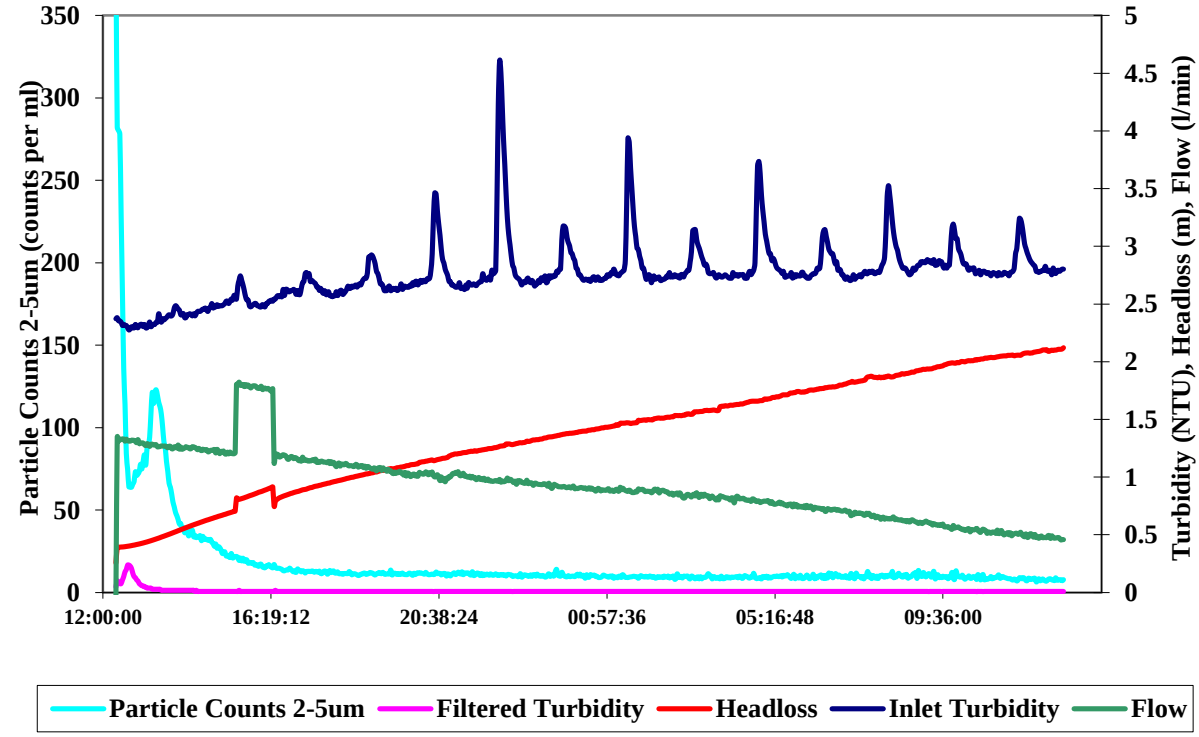


Figure 94 50% Flow change at 3 hours using 0.05 mg/l AH912 Run 2 pH 4.5 and 7°C, November 2004.

Part 7.4.1 50% Flow change at 6 hours using AH912

The particle shedding effects of flow change is often heightened at the latter stages of the filter run as particles can shed considerably at this stage with only a small magnitude flow change, partially due to the media having collected more particles than in the early stages in the run (Fitzpatrick *et al.*, 1999). Figure 95 shows that some filtered turbidity and particle count breakthrough occurred during the run, in the final stages. This breakthrough was more apparent in the particle count trend which showed an increase from 11 to 50 counts/ml. The turbidity increase was less, from 0.009 to 0.1 NTU. The breakthrough started well after the flow change at approximately 12 hours into the run, and appeared to improve at the end of the run.

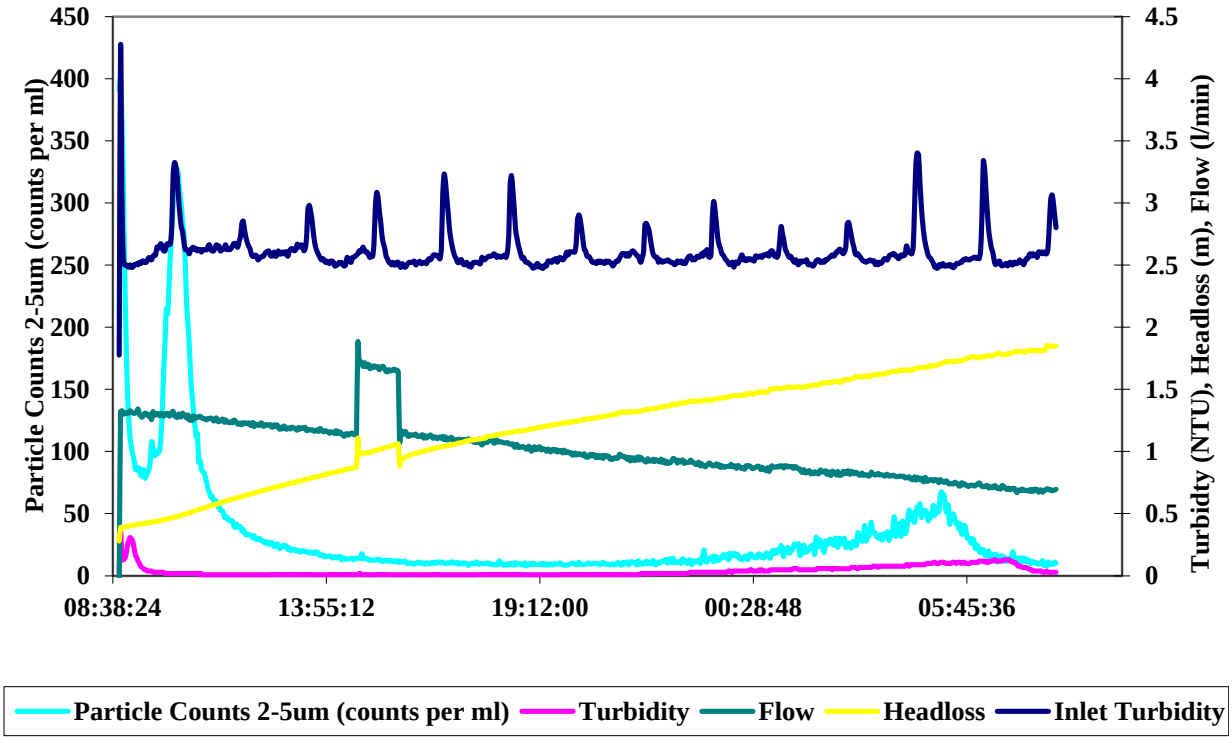


Figure 95 50% Flow change at 6 hours using 0.05 mg/l AH912 Run 1 pH 4.5 and 7°C, November 2004.

The absence of breakthrough at the point of what was a considerable flow change at cold temperatures, is an indication that the deposited floc was strongly attached to the media grains, and the new incoming floc was also capable of adherence to the deposited floc and/or media grains. Considering also that the pilot filter could not achieve an acceptable baseline filtration performance without breakthrough at this time as shown in the run dosed with 0.005 mg/l polymer (figures 95 and 96) – the increased robustness of the filtration performance has

to be attributed to the polymer dose and its effects on the floted floc carryover. The ability to withstand flow change without particle shedding is a very useful attribute as the risk of passage of cryptosporidium is greatly reduced, and the overall plant robustness to changes in hydraulic demand is improved. The breakthrough observed later in the 2 runs could have been due to the filter reaching a point where the media pores were clogged to such a level whereby the interstitial velocity became significant and the shear stresses too great and particles were shed from the media.

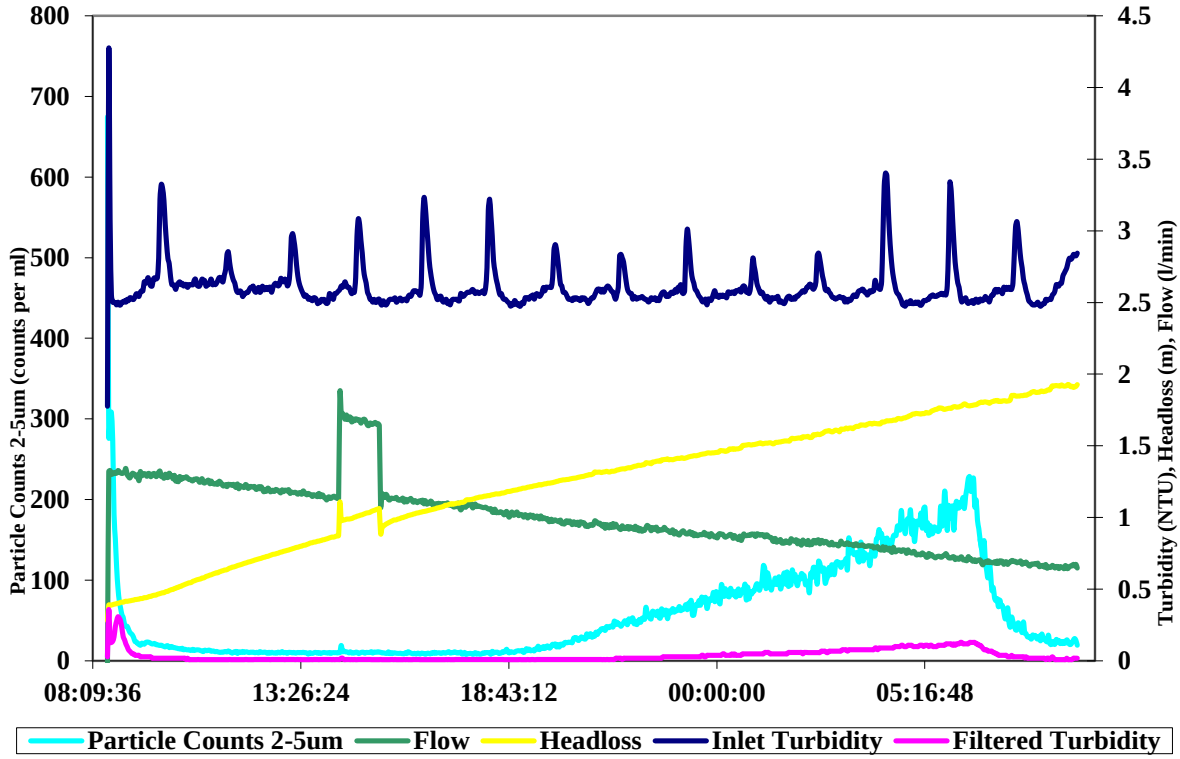


Figure 96 50% Flow change at 6 hours using 0.05 mg/l AH912 Run 2 pH 4.5 and 7°C, December 2004.

Part 7.5 Pilot filter performance using AN905

Figures 97 and 98 show a very similar trend in filter performance compared to the results in part 7.4. This is with respect to the increasing filter run length and filtered water quality as the polymer dose increased. The flow change tests were not repeated with AN905 as the decision was made to perform the full-scale plant trial using AH912. This decision was based on the resource time available and the good performance observed with AH912.

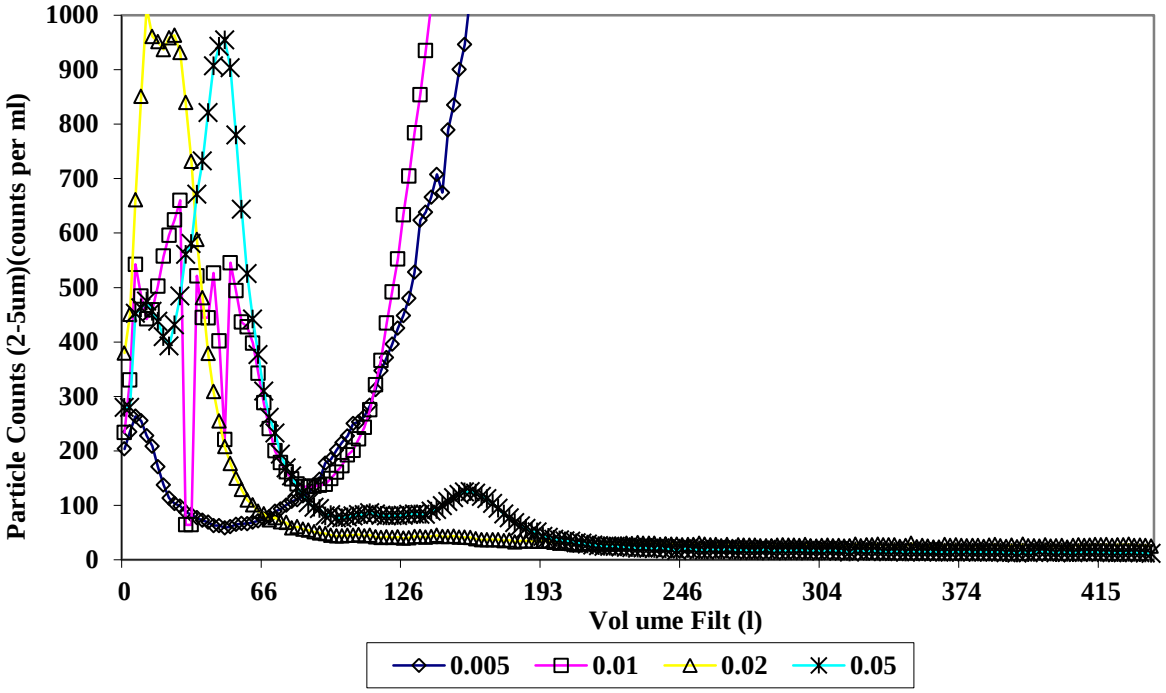


Figure 97 Filtered particle Counts using AN905 pH 4.5, 7°C, December 2004

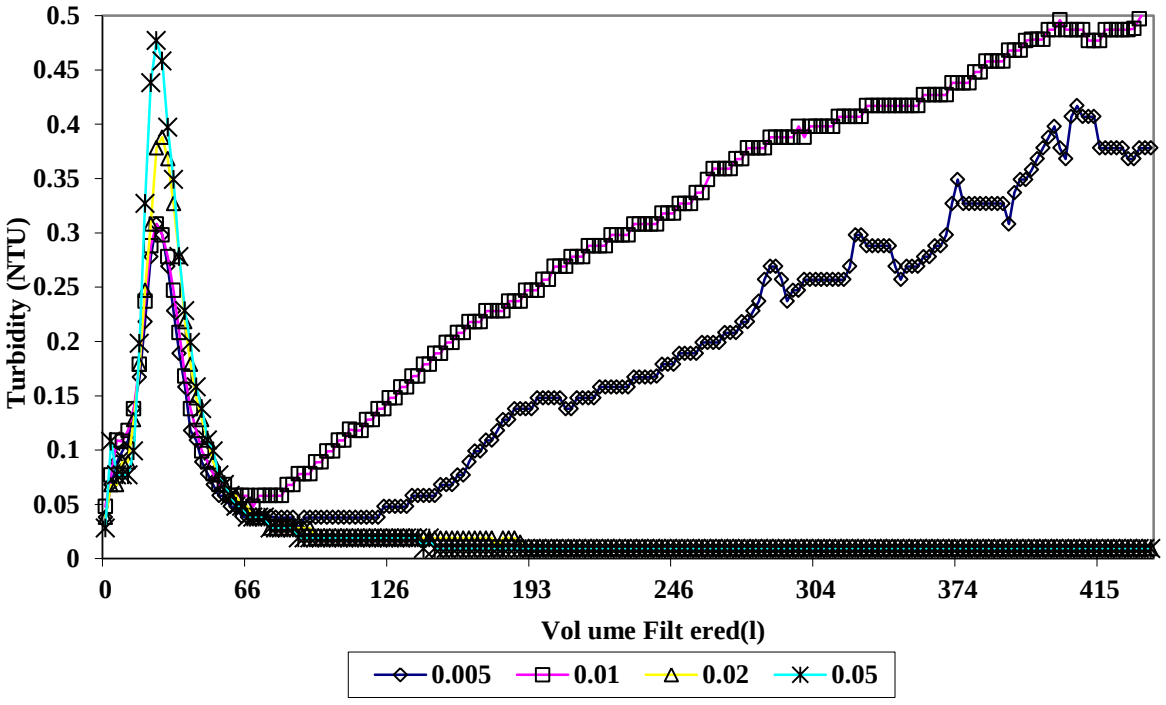


Figure 98 Filtered turbidity using AN905 pH 4.5, 7°C, December 2004

Part 7.6 Summary of pilot filter trials using AN905 and AH912

Figure 99 shows a comparison of the filtered water quality from the two polymer trials. Overall both filtered turbidity and particle counts are observed to decrease as the concentration of both polymers is increased. The filtered particle counts was generally lower using AH912 throughout the lower dose range 0.005-0.02 mg/l, but at the highest dose of 0.05 mg/l the performance was slightly worse than AN905 at the highest dose.

This was also reflected in the filtered turbidity trends. The power failures that happened during the start of the trial with AN905 at 0.01 mg/l were likely to have contributed to the slightly higher particle count and turbidity trends observed, as the pilot plant feed pump started and stopped.

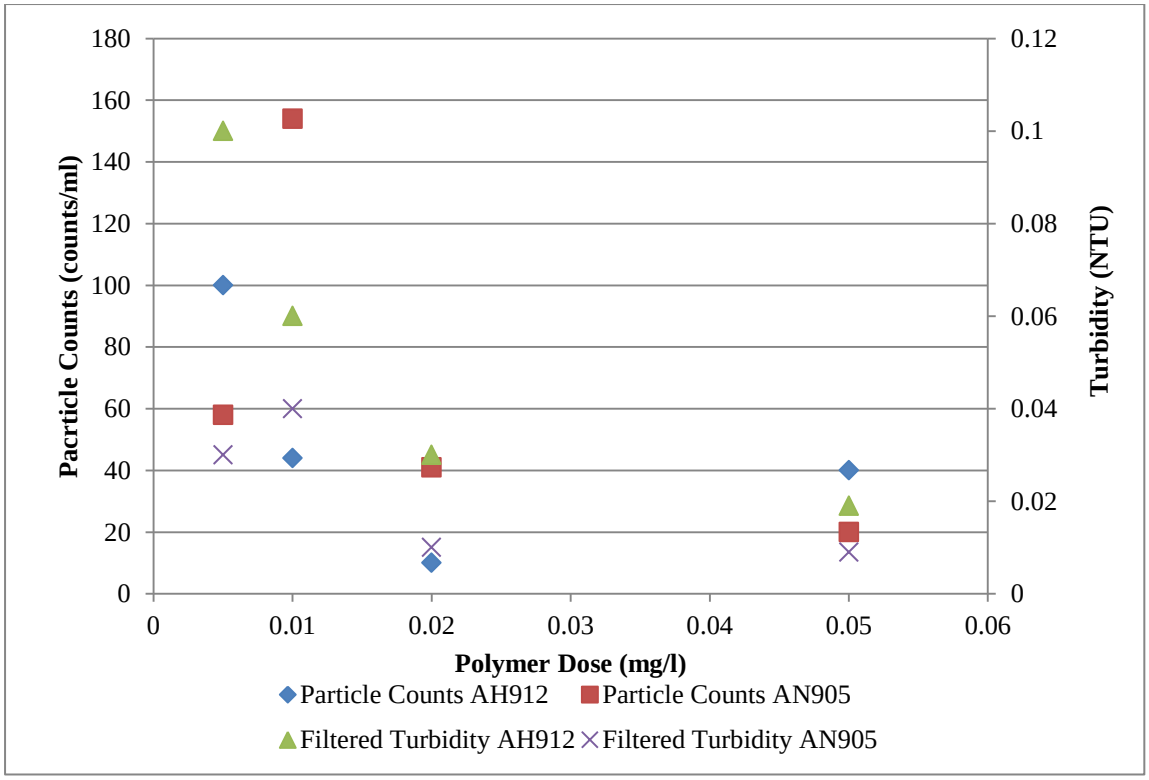


Figure 99 Pilot plant baseline filtered particle counts at 450l (2-5µm) and turbidity using AH912 and AN905, November-December 2004, 7°C, pH 4.5.

Figure 100 shows the rate of headloss development during the two trials plotted alongside the FI_{ref} parameters obtained from the breakage jar tests using AH912. The anionic polymer dosed systems resulted in a slightly greater rate of headloss development than the non-ionic polymer systems despite a lower influent floted water turbidity. The correlation between FI_{ref} and the rate of head loss development during the trial using AH912 was linear and implies that FI_{ref} was a good approximator of the floc size going onto the filter.

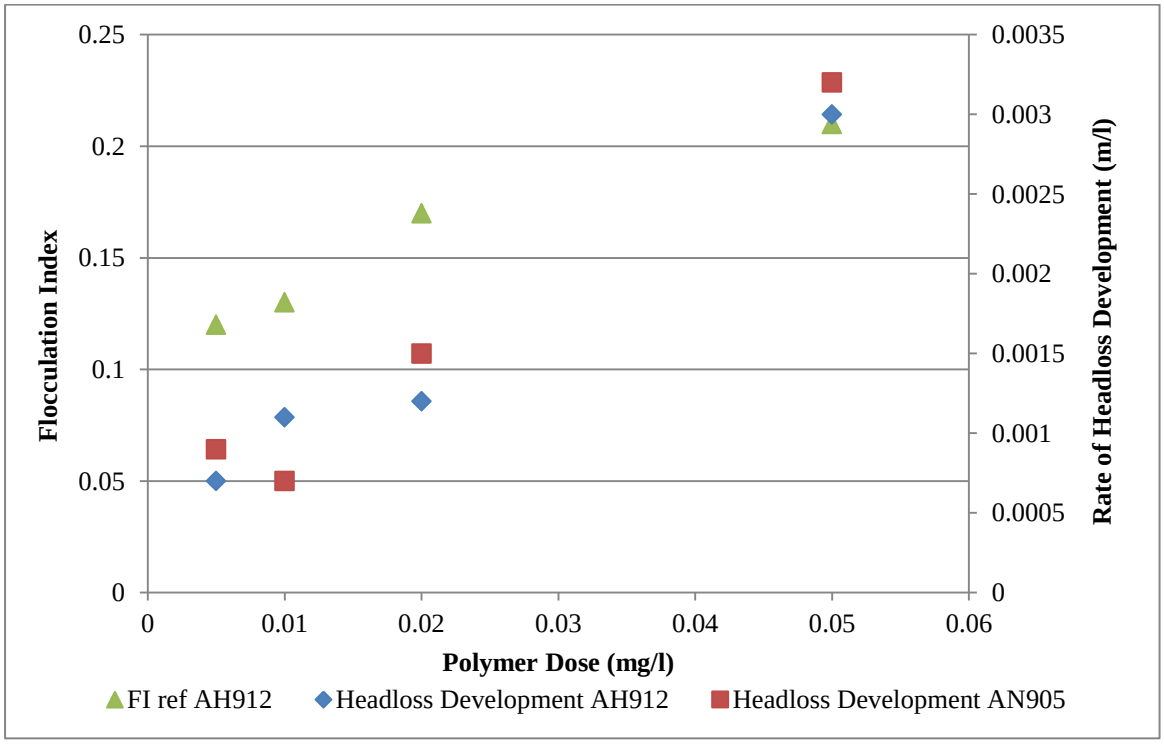


Figure 100 Pilot plant filter rate of headloss development using AH912 and AN905, November-December 2004, 7°C, pH 4.5, Zeta Potential +3.4 to +4.1 mV.

Breakage jar tests using the PDA and a selection of flocculants were carried out and the best performers were chosen to dose onto the pilot filter plant. The two chosen flocculants were AN905 and AH912, and a range of doses (0-0.05 mg/l) were applied to the pilot filter and the filter performance was monitored. Breakage jar tests were carried out on water taken from the mixing tank during each run in order to assess the dynamic flocculation parameters at each dose and relate to filter performance. The removal of humic substances was also monitored by means of hourly DOC and UV_{254} absorbance samples. The pilot filter performance was continuously monitored by means of online trending of headloss, flowrate, inlet and outlet turbidity and effluent particle counts.

Some important results were obtained, which are as follows:

- Both flocculants showed an increased removal of humic substances as the dose increased with a maximum removal obtained at the highest dose of 0.05 mg/l.
- Filter performance in terms of effluent particle counts and turbidity showed considerable improvement with both flocculants as the dose increased. The improvement was consistent and filter run time increased with polymer dose, with the higher doses not showing breakthrough throughout the run.
- Headloss build-up on the filter showed a linear trend during the run time. The rate of increase in headloss with time was proportional to polymer dose for both polymers. The rate of increase in headloss was also similar for each flocculant but slightly lower with AH912.
- Breakage jar tests performed using the pilot plant mixing tank water and AH912 showed high floc reformation factors, indicating reversibly formed floc. The values of FI_{max} generally showed an upward trend as the polymer dose increased, suggesting that the floc size was larger as the dose increased. The values of FI_{ref} also increased, suggesting that the floc at the end of the jar test was larger than the control systems. Floc strength factor also exhibited the same trend that has been observed throughout this work, and that is decreased floc strength factor as the floc size increased.
- The lower turbidity during the trial using AN905 prevented any dynamic flocculation parameters being computed as the flocculation index curves were too noisy to interpret. This suggests that there is a low turbidity range below which the PDA cannot to be used to monitor flocculation as there wasn't sufficient particulate present to obtain a continuous reading.

Both flocculants showed the potential to increase filter run time before breakthrough and in some cases eliminate it altogether. There wasn't sufficient resource to test both flocculants on the main plant so the flocculant which was tested by means of the flow change tests was used which was the non-ionic flocculant AH912. The flow change tests showed that a dose of 0.05 mg/l AH912 was successful at preventing breakthrough at the time of a 50% flow change, both after 3 hours and after 6 hours.

Part 7.7 Full-scale plant trial using AH912 at Albert WTW

The previous pilot plant trials using the two flocculants were successful at preventing filter breakthrough and improving filter run time, so it was logical to carry out a dosing trial on the full scale plant to assess the benefits. There are many issues to consider during the scale-up of the pilot plant to the main plant as summarised below:

- The pilot filter plant was a reduced bed depth in comparison to the plant filters. The pilot filter plant was 0.45 m bed depth compared to 0.9 m bed depth on the full-scale plant. The media was the same and taken from one of the plant filters.
- Hydraulic conditions for mixing the polymer would be completely different. The pilot plant setup was designed to optimise mixing by using a dilute stock solution of polymer. The more dilute the stock concentration, the more likely the solution will mix with the water. The pilot plant mixing tank also had an in-built paddle stirrer that would offer better mixing than the proposed plant solution of dosing into the filter inlet channel via a sparge-bar counter-current to the inlet weir.
- The time taken to re-form the floc before it starts filtration is unlikely to be comparable as the pilot plant mixing tank was situated directly above the filter column whereas on the full-scale plant the water flowed along a 90m channel before entering the filters.

This means that the full scale plant dosing design, and the actual applied dose would need to be carefully established in order to achieve the beneficial results indicated by the pilot filter plant. The full scale plant trial was started at the end of this work but due to resource restrictions, the monitoring of the results fell outside of the scope of this work. A copy of Yorkshire Water report on the full-scale plant polymer dosing is included in appendix 5. This shows that the dosing of up to 0.05 mg/l AH912 into the floted water via a sparge-bar resulted in increased filter run length and consequently increased the hydraulic output of Albert WTW by approximately 5-7 Ml/day.

Part 7.8 Conclusions

The work carried out onsite at Albert WTW using the four flocculants and the pilot plant experimental apparatus illustrated in Chapter 3 was used to identify if the filter breakthrough problem at Albert WTW could be solved by improving the floc physico-chemical characteristics prior to filtration. The PDA results generated from the breakage jar tests carried out on the main plant DAF outlet water showed two important points:

1. The PDA can be used to monitor re-flocculation of micro-floc that has been carried over from the plant DAF outlets. This has not been reported before as the PDA has not been used to assess re-flocculation of partially treated water. There does however appear to be a low turbidity cut-off below which the flocculation curves were not usable. This suggests that with further study and optimisation, the PDA could be developed into an online tool.
2. It is possible to dose small concentrations of flocculant into DAF outlet water and achieve an increase in floc size, and generate reversibly formed floc with a F_{ref} =1. Whilst polymers have been used to improve separation processes for many decades, the application to DAF outlet water is a novel one.

Filter outlet water quality in terms of particle counts and turbidity was found to improve significantly with flocculant dose and filter breakthrough was prevented using certain doses of the two polymers applied to the filter. This meant that filter run length was considerably extended using the flocculants, without causing extremely high head-losses at mid-range doses of flocculant. The ability of the filter to withstand hydraulic shock caused by flow changes was also tested with the AH912 dosed system and the following was concluded:

- The polymer dose of 0.05 mg/l prevented filter breakthrough as measured by turbidity and particle counts during the applied flow changes at 3 hours and 6 hours into the run.
- The PDA results indicated that the main effect of the polymer dosing was to increase the floc size, and it is concluded that this parameter was the most important in explaining the improved filter results. Polymer dose was proportional to FI_{max} which in turn was proportional to filtered water quality and rate of increase in headloss.

Chapter 8 Overall Discussion

Part 8.0 Introduction

In this chapter the findings from the four results chapters are compared and contrasted in order to evaluate the research project as a whole, and present the insights gained. The experiments in Chapters 5 to 8 set out to use a combination of jar test, and pilot-scale experiments to investigate how floc physico-chemical properties are affected by variables such as coagulant/flocculant type, dose and pH, and what the subsequent impacts on NOM removal and filter performance were.

Part 8.1 Primary coagulation jar tests - discussion of main findings and insights

Part 8.1.0 Preliminary investigations into the effect of coagulant type on NOM removal and floc properties

The experiments in Chapter 4 were centered on defining characteristics for a system based on the coagulant type, and identifying potential for improving floc strength at the primary coagulation stage by using polymeric additives. This proved unsuccessful in terms of identifying a system with improved floc properties as well as good NOM removal performance. On this basis the matrix for the 2nd set of experiments was based around exploring the possibilities to alter floc properties of ferric sulphate based coagulation systems by changing coagulation pH and dose.

Part 8.1.1 The effect of coagulation pH on NOM removal and floc properties

In these experiments unlike the first set in Chapter 4, the degree of charge neutralisation was measured in the form of zeta potential measurements on the settled water. The jar test matrix was also changed from a 300ml plastic beaker to a conventional 5 1 litre jar test Aztec flotation unit. This made direct comparisons between the data from Chapter 4 and 5 very difficult due to the different shear regimes between the two jar testers. However it is possible to compare and contrast the main findings. The main findings from Chapter 5 are best discussed under the following sections:

1. NOM removal performance and pH/Ferripol XL dose

The findings from all three sets of jar tests showed that NOM removal as measured by UV_{254} absorbance was very similar and good at pH 4.5 and pH 6.5, but poor at pH 3.5. The Fe/DOC ratio studied at each coagulation pH condition was 1.2, 1.7 and 2.02. At coagulation pH 3.5 the impact of increased Fe/DOC ratio on the residual UV_{254} absorbance was very slight. The fact that flocculation was observed at coagulation pH 3.5 and that there was some NOM removal (>50%) indicates that some fraction of the humic substance was reactive under acidic conditions. Overall the results showed that within the range of Fe:DOC used the optimum coagulation pH for NOM removal was mostly pH 4.5 which is consistent with the literature. Coagulation pH 6.5 performed well within the range of Fe:DOC applied but is not thought to be a viable pH to operate a full-scale plant as the quantities of sludge to process would be significantly higher as would the chemical costs.

2. Floc properties and pH

The impact of increasing the Fe/DOC ratio on the floc size as measured by FI_{max} was negligible between 1.2 and 1.7 at coagulation pH 3.5 and 4.5 but increased considerably as the Fe:DOC increased to 2.02. The visual results generated from the tests at pH 6.5 also indicated that there was an increase in floc size – the PDA results generated from pH 6.5 were not thought to be representative in terms of floc size. It has been noted by Yu *et al*. (2010) that the PDA floc index results (and other similar light scattering techniques) in the sweep flocculation mode are subject to error as the floc size as measured by the floc index may not be proportionate to the actual floc size due to the mechanism of formation of the primary particles. The particulate formed during "sweep" flocculation is primarily hydroxide sols that have adsorbed NOM attached, these particles are thought to have a low refractive index, and can have extinction cross sections much less than their projected area.

The mode of NOM removal is believed to be dominated by precipitation of metal hydroxides at pH >6 (Gregor *et al*., 1997). This implies that the mode of coagulation at pH 6.5 should have been that of "sweep flocculation" but the data showed that at pH 6.5 the zeta potential tended towards 0 mV as the Fe:DOC ratio increased. The zeta potential trend suggested charge neutralization as the mode of coagulation, rather than "sweep flocculation" but the PDA data did not agree with visual observations at Fe:DOC of 2.02.

The flocculation rate at Fe:DOC ratio of 2.02 was observed to tail off in comparison to the 1.2 and 1.7 thereby supporting a different mechanism for coagulation – formation of the hydroxide sols is reputed to be rapid and therefore "sweep flocculation" systems should flocculate faster than "charge neutralization" systems. The flocculation rate using Fe:DOC ratio of 2.02 would have been expected to be quicker than the Fe:DOC systems of 1.2 and 1.7 if "sweep flocculation" was the mode of operation. The zeta potential data actually suggests that "sweep flocculation" occurred at Fe:DOC ratio of 1.2 and 1.7 but "charge neutralisation" was the more likely mechanism at Fe:DOC ratio of 2.02. It is also worth noting that the degree of UV_{254} absorbance removal was highest at this condition. If the zeta potential measurements and UV_{254} absorbance removal data using Fe:DOC ratio of 2.02 were reviewed in isolation from the PDA data, then the results would suggest charge neutralization as the mechanism. In this case, the PDA data indicated that the mechanism was sweep flocculation. There may be a case to support the two processes occurring concurrently at this pH. There is a lack of literature studying these parameters outside of the optimum coagulation pH of 4.5 and so it is difficult to validate against previous results. More study in this area would verify whether this is a repeatable result, although ultimately a coagulation pH of 6.5 would be costly and would most likely increase the solids loading on the downstream processes. In this set of experiments the flocculation rate was heavily influenced by coagulant dose at each pH condition but the dose was independent of UV_{254} absorbance removal. At the lower Fe:DOC ratios the difference in flocculation rate at each pH condition was minimal but as the Fe:DOC ratio increased the difference became more marked and the rate increased. This effect has also been observed by Jarvis *et al*., (2004) who noted that increased Fe:DOC had a dominating impact on the flocculation rate, and also floc size.

The range of coagulant doses used in this set of experiments compared to the previous set was smaller and much closer to the optimum dose – therefore the flocculation rate was not such a system-defining parameter as was the case in the first set of tests when the coagulant dose range was larger. This is an important factor to include when designing coagulant dose optimization strategy so that effort can be focused on the most influential parameters.
The effect of increasing Fe:DOC on floc size as measured by FI_{max} was also noted to be similar to the findings of Jarvis *et al*. (2004) who used a Mastersizer 2000. As the dose increased relative to the NOM concentration, the steric and repulsive effects of the NOM were reduced thereby enabling faster floc growth and larger flocs.

The data presented in part 5.6.5 suggested that there was a threshold Fe:DOC ratio independent of the pH condition between 1.7 and 2.0 whereby the floc size was influenced by the increased coagulant dose. There was little change in FI_{max} between Fe:DOC of 1.4 and 1.7, although the flocculation rate was influenced strongly throughout the range of Fe:DOC. A greater range of Fe:DOC would have been beneficial in identifying the threshold for increase in FI_{max}. In this work the findings of Duan and Gregory (2002) and Jarvis *et al.* (2004) at optimum pH 4.5, with respect to the relatively smaller size of "charge neutralization" flocs compared to bridging and sweep flocs was confirmed as true for coagulation pH 3.5 and 6.5.

3. Zeta potential and pH/Ferripol XL dose

Work by Sharp *et al.* (2006) on the same raw water source provided evidence for an operational window for zeta potential, within which NOM removal is optimal. This window was documented to be -10mV to +3 mV. The results from Chapter 5 of this work also confirm the operational window and provide some evidence to extend the upper bound to +4 mV. Fe:DOC ratio has already been shown to have had an impact on flocculation rate, and FI_{max} but there was no appreciable impact on NOM removal at each pH condition due to the increased Fe:DOC ratio. The influencing factor in NOM removal during these tests was seen to be coagulation pH and NOM removal mechanism.

The tests at coagulation pH 3.5 resulted in a system which was on the upper edge of the operational window for zeta potential and consequently had poor NOM removal performance. At pH 3.5 the likely interaction of the coagulant and NOM would have been patchwork agglomeration where only partial neutralisation is required to form floc (Ratnaweera *et al*., 1999) and the surface charge is not required to have been neutralized fully. The floc reformation factor was observed to increase in the more positive zeta potential systems on the outside of the operational window which suggests that patchwork agglomeration is an influencing factor in the floc reformation ability at this pH condition. At coagulation pH 6.5, some systems with more negative zeta potentials (<-10 mV) existed with sub-optimal NOM removal (>5 abs/m) and higher floc reformation factors than observed at pH 4.5. The mechanism for NOM removal at negative zeta potential values is thought to be due to polymer bridging between the high molecular weight material (Ratnaweera *et al*., 1999).

The mechanisms of both polymer bridging and patchwork agglomeration could be said to be more supportive of floc reformation as reflected in the generally higher floc reformation values obtained at zeta potential >4 mV and zeta potential <-10 mV. The mechanism for NOM removal at pH 4.5 is reputed to be mainly charge neutralization (Duan and Gregory, 2002) which in these experiments consistently resulted in the lowest floc reformation factors. The data generated from the experiments in Chapter 5 wasn't comprehensive enough to fully substantiate the relationship between floc reformation and zeta potential as there were no systems with a zeta potential within the range -10mV to +2 mV. The results from Chapters 4 and 5 have substantiated the work of others such as Jarvis *et al.*, (2004) and Duan and Gregory (2002), and also expanded further to include the effects of operating outside of the literature quoted optimum pH for ferric salts of pH 4.5. The impact of increasing Fe:DOC ratio on the dynamic flocculation parameters FI_{max}, floc strength factor and flocculation rate appear to be consistently linked. The most commonly changed parameter on a full-scale water treatment plant is the coagulant dose and therefore the Fe:DOC ratio, and it is useful to examine the effects of altering this key ratio on plant performance.

Part 8.1.2 The effects of Fe:DOC ratio on floc properties and NOM removal

The jar tests experiments presented in Chapters 4 to 6 had a common theme running through them, which was the impact of altering Fe:DOC ratio on floc properties. One element of this work involved assessing the impact of Fe:DOC ratio on floc size (FI_{max}) , floc strength factor (F_{brk}) and floc reformation factor (F_{ref}). There are complexities associated with direct comparison of the absolute values of the derived parameters between the chapters due to the following:

- Different jar test shear regimes in Chapter 4 compared to Chapter 5. Vessel size and stirrer dimensions different therefore energy dissipation rates at breakage state not equivalent.
- Different floc origin (partially formed floc from DA20 flocculator inlet) in Chapter 6 compared to Chapters 4 and 5.

- Raw water NOM character (as qualified by SUVA) was slightly variable between the experiments. This meant that the dominating fractions in the Chapter 5 experiments were high MW hydrophobic fractions and in Chapters 4 and 6 were more of a mixture of hydrophilic and hydrophobic components as according to table 48 from Edzwald and Tobiason, (1999).

SUVA	Composition	Coagulation	DOC Removal
>4	Mostly aquatic humics. High hydrophobicity, High MW	NOM Controls. Good DOC removal	>50% for Alum >50% for Ferric
2-4	Mixture of aquatic humics and other NOM. Mixture of hydrophobic and hydrophilic NOM, mixture of MWs	NOM influences. DOC removals OK	25-50% for Alum Little greater for Ferric
<2	Mostly Non-Humics. Low hydrophobicity. Low MW	NOM has little influence. Poor DOC removal	<25% for Alum Little greater for Ferric

Table 48 Guidelines for the nature of NOM and expected DOC removal by coagulation (Edzwald and Tobiason 1999)

This prevents the direct comparison of the absolute values of the floc properties between the systems in Chapters 4 to 6 but still allows for comparison and contrast of the overall impacts of the controlled variables such as Ferripol XL dose (or Fe:DOC ratio) on floc physico-chemical properties. One of the common themes running between the experiments in Chapters 4 to 6 was the impact of coagulant dose relative to DOC content on floc physico-chemical properties at coagulation pH 4.5 – this was studied in two sets of jar tests and pilot plant filtration experiments.

The earlier discussion with respect to the nature of the NOM in the raw water between the tests in Chapters 4 to 6 revealed that the raw water SUVA was slightly different between the pieces of work but should act in a broadly similar way with the coagulant as DOC removal is still reported to be good with ferric salts (Edzwald and Tobiason, 1999). The SUVA calculated from the data in Chapters 4 and 6 was also higher than the range reported by Parsons *et al.* (2003) to be dominated by the difficult to remove hydrophilic compounds, and therefore were thought to behave similarly with the coagulant.

The main findings relating to the impact of increasing the coagulant dose (Ferripol XL or ferric sulphate) can be found in Chapter 4. The experiments in Chapter 4 were performed within a broad dose range, whereas the experiments in Chapters 5 and 6 were narrower dose ranges with over-dosing studied in Chapter 5 and a narrow range around the optimum in Chapter 6. The impact of increased coagulant dose on floc size and flocculation rate within the broad dose range, was similar to that observed in Chapters 5 and 6 using a narrow dose range. The magnitude of the change in FI_{max} was in some cases not found to be sensitive to changes in dose, for example; in the Chapter 4 experiments FI_{max} was very similar using 3.5 mg/l as Fe^{3+} or 7.1 mg/l as Fe^{3+}. This was also the case at the lower doses of Fe:DOC ratio used in Chapter 6 also, and an increase in Fe:DOC ratio of 0.7-1 resulted in very little change in floc size. In Chapter 5 there was also little change in floc size between 1.4 and 1.7 Fe:DOC, and then a more marked increase between 1.7 and 2.02 Fe:DOC.

There seemed to be a threshold Fe:DOC ratio of between 1.2-1.7, below which there was little change in FI_{max}, and above which there was a marked increase in FI_{max}. A study carried out by Jarvis *et al*. (2005) using a Malvern Mastersizer 2000 on the same raw water source found that if the coagulant to DOC ratio was maintained at around 1, then the floc size, strength and structure was improved as the steric repulsive effects of the NOM were minimised. The work by Jarvis *et al*. (2005) postulated the theory that as the ratio of organic matter to coagulant dose increased, the steric repulsive effects of the NOM dominated. This could also explain why the lower Fe:DOC ratios used in these experiments didn't result in increased floc size, as the dose was not high enough to have overcome the steric repulsive effects and the quantity of bridging bonds formed was lower, and thus the floc size was smaller. Broadly speaking this work confirmed the findings of Jarvis *et al*. (2005) and also went on to relate Fe:DOC ratio to filter performance which is discussed later in this chapter. Table 49 summarises the main findings from the jar tests in Chapters 4 to 6.

Chapter	Coagulant system parameters	Dose range	Controlled variable	Impact on floc properties as Fe:DOC increased	Impact on zeta potential as dose increased	Impact on NOM removal as dose increased
4	Ferric Sulphate (22°C) SUVA = 3.8 m^{-1}L/mg C* *batch 1 and 2	Broad (3.5-14 mg/l as Fe^{3+})	Dose (0.4-1.8 Fe:DOC)	Size increased up to optimum dose for NOM removal, then decreased. R_{FI} changed in parallel with size	Not measured	Increase by 35% as dose tended towards 10.6, then decreased
5	Ferripol XL (15°C) Raw water SUVA = 4.9 m^{-1}L/mg C Raw water zeta potential -15 mV	Narrow over-dose (10-14 mg/l as Fe^{3+})	Fe:DOC (1.4-2.02)	Little change in size between 10 and 12 mg/l as Fe^{3+}, then increase as dose increased to 14 mg/l as Fe^{3+} No change in floc strength factor Slight decrease in floc reformation factor R_{FI} increased in parallel with size and dose	General increase (-0.6 mV to 3.7 mV settled)	Very little change
6	Ferripol XL (18°C) Raw water SUVA = 3.6 m^{-1}L/mg C Raw water zeta potential (-17.7 mV to -15.4mV)	Narrow (6-11 mg/l as Fe^{3+})	Fe:DOC (0.7-1.2)	Little change in size between 0.7-1, then increase as dose increased to 1.2 Slight reduction in floc strength factor as dose increased Higher F_{ref} values obtained at mass ratio of 1:1 coagulant to DOC	General increase with dose, more pronounced at 1.2 (-12.4 mV to 2.4 mV flocculated)	Increase by 10% over dose range

Table 49 Summary of primary coagulation jar test results – impact of Fe:DOC ratio on floc properties, charge and NOM removal

An interesting result observed from the results in Chapter 5 was the lack of impact of dose on NOM removal. The impact of increased Fe:DOC ratio on floc size is thought to be due to the balance of the steric repulsive effects of NOM being overcome by the coagulant dose, thereby increased ratios lead to increased flocculation rates and floc size. In this case the size increased with Fe:DOC ratio which is supportive of the concept that the NOM removal should have also increased. However it is possible that as the raw water was dominated by the easy to remove hydrophobic components, the relationship between dose and NOM removal is less important when dosing enough to overcome the repulsive effects. Therefore the impact of dose on NOM removal could be less significant within an optimal dose range. It is also possible that the optimum dose was not achieved during these experiments, and the dose range applied was too narrow to observe changes in NOM removal performance. A review of previous work shows that for iron based coagulants, optimum NOM removals are seen around or slightly below an iron (Fe) to organic carbon mass ratio of one to one (Eikkibrook,1999; Vilge-Ritter *et al*., 1999; Cheng *et al.*, 2002; Fearing et al., 2004).

Part 9.1.4 The effects of Fe:DOC ratio on floc strength and reformation factors

Another common theme investigated in Chapters 5 and 6 was the relationship between coagulant dose, NOM removal and floc strength and reformation factors at coagulation pH 4.5. The results from Chapter 4 included calculation of floc strength and reformation factors, but were more focussed on comparison between coagulant types rather than purely assessing the impact of dose relative to NOM content. The most useful comparisons to be made in this regard therefore were those between Chapters 5 and 6 relating to the effect of Ferripol XL dose on floc strength and reformation factors and NOM removal. In Chapter 5 the impact of coagulant dose was observed to increase FI_{max} from 0.34 to 0.6 over the dose range applied, albeit with only a slight increase between 1.4 and 1.7 Fe:DOC, but this did not correspond to a change in floc strength factor. Usually under given shear conditions larger flocs are reported to have decreased floc strength by breakage test type methods (Jarvis *et al.* 2005), and so this result is surprising and requires further investigation to determine whether this was due to the high Fe:DOC ratios of >1 or different breakage mechanisms

In Chapter 5 the floc reformation factors showed a slight decrease (10%) as the Fe:DOC ratio increased to 2.02, whereas in the tests in Chapter 6 floc reformation factor appeared to increase at a mass ratio of coagulant to DOC of 1. It is possible that the experiment using a Fe:DOC ratio of 2.02 was operating at over-dose conditions and this is supported by the positive zeta potential of +3.7 mV which tends towards the upper bound for good operation found by Sharp et al. (2006) of -10mV to +3mV. This may have impaired the re-growth process by re-stabilisation of part of the NOM and thereby reduced the floc reformation factor. The apparent increase in floc reformation factor observed at Fe:DOC ratio 1 in Chapter 6 could have been due to structural changes in the nature of the floc as observed by Jarvis *et al.* (2005). They noted that floc structure was much improved at a ratio of DOC:Fe of 1, mainly thought to be due to a reduction in the bridging bonds formed at higher DOC ratios, and the resultant changes in floc from open loose structures to more compact structures. The jar tests in Chapter 6 revealed a more conventional trend of increased floc size as Fe:DOC ratio increased from 1 to 1.2, with a corresponding decrease in floc strength factor which wasn't observed in Chapter 5 tests. Overall the findings in this work broadly concur with the findings of Jarvis *et al.* (2005) with respect to the increases in floc size with increased Fe:DOC ratio, and also suggest that there is an optimum Fe:DOC ratio for increased floc reformation of 1.

Part 8.2 Pilot scale filtration experiments– discussion of main findings and insights

There were two sets of pilot scale filtration experiments carried out in this work, both of which were centred on examining the impacts of floc properties on filter performance, but using water from a different treatment stage. The experiments in Chapter 6 used raw water and the DA20 flotation plant to examine the impacts of increasing the Fe:DOC ratio on filter performance with a pilot-scale plant operated at coagulation pH 4.5. The experiments in Chapter 7 used Albert WTW pre-filtered water and focussed on the impacts of altering floc properties on filter performance by dosing flocculants prior to the filtration stage. The Fe:DOC ratio on the main plant ranged from 1.3 to 1.7 during the filter experiments. The findings from these experiments are best discussed separately.

Part 8.2.0 The effect of Fe:DOC on floc properties and filter performance

In these experiments, a 1000ml sample of water was withdrawn from the DA20 flotation pilot plant and subjected to the same breakage jar test procedure as used in previous chapters. The reason for this was to allow for the difference in flash mixing arrangements between the jar test (paddle type mixer) and the DA20 (static mixer). It was thought that a fairer comparison was to remove the initial mixing condition difference by taking the samples straight from the DA20 flocculator inlet. It is acknowledged that the actual energy dissipation rates were not studied or quantified in these experiments, and a more rigorous approach would have been to account for the actual energy dissipation within the jar tests as compared to the pilot plant. However the method used was valid in terms of qualifying changes in floc characteristics as the Fe:DOC ratio was increased throughout the pilot plant trials. The approach used also removed any potential discrepancy between the conditions on the pilot plant (dose, pH) and the laboratory jar tests. In the tests in Chapter 6, the floc strength factor reduced as Fe:DOC ratio increased from 0.7-1.2 with a corresponding increase in FI_{max}. Floc strength is usually observed to decrease as floc size increases as suggested in the literature (Jarvis et al, 2005) and earlier results in this work. The impact of increased Fe:DOC ratio on the NOM removal as measured by UV_{254} absorbance and DOC was seen to improve the pilot plant performance, and the range of floted water zeta potentials achieved were mostly within the operational window of -10 mV to + 3 mV as reported by Sharp et al, 2006.

Some runs resulted in floted water zeta potentials outside of the lower bound of this range without compromise to residual NOM levels, but filtration performance was observed to deteriorate under these conditions. The raw water zeta potential during the jar tests in March 2004 was -15 mV, and during the pilot plant trials in May-August 2004 varied between -15 mV to -17.7 mV. The proportion of the difficult to remove hydrophilic components were likely to have been slightly higher in the DA20 pilot plant trials compared to Chapter 5 tests, as the SUVA was tending towards < 4 m^{-1}L/mg C , and the threshold below which the hydrophilic components are thought to dominate is 3 m^{-1}L/mg C (Parsons *et al*, 2004). The water quality during the DA20 pilot plant trials presented in Chapter 6 should have been more difficult to treat than the raw water in Chapter 5 as the raw water SUVA was lower, but the UV_{254} absorbance removal achieved over the Fe:DOC range 0.7-1.2 was better which suggests that the water was just as treatable.

One of the key elements to this work in Chapter 6 was to examine the relationship between floc physico-chemical properties and NOM removal performance, and in particular to assess the impact on filter performance.

This is of prime importance as the filtration stage is the key solid-liquid separation stage and responsible for removal of pathogenic elements such as Cryptosporidium parvum. Rapid gravity filter performance is often the pinch-point of the treatment works, as situations can occur whereby the filters perform badly (either turbidity breakthrough and/or high headloss) and require back-washing more frequently which disrupts the process even further. The jar test part of the work established that there was little difference in floc size (FI_{max}) between Fe:DOC ratio of 0.7-1, but then a step-change by a factor of 2 occurred when the ratio increased to 1.2. The floc in the final set of trials exhibited the lowest floc strength factor of the trials, in accordance with the largest size but despite this re-grew to a higher magnitude of $FI_{ref.}$ The floc reformation factor was still low as the floc was proportionally larger to start with. This suggests that the floc formed at Fe:DOC ratio of 1.2 was most likely to be larger than the lower ratios, and therefore the carryover to the pilot filter inlet would have also been larger. The PDA was not used to measure the floc size at the filtration inlet as initial trials found that the reading was difficult to interpret, presumably as volume and concentration of particles were on the lower limits for detection at the time of the trial.

It was therefore not possible to accurately relate the floc size in the jar test to the floc size entering the pilot filter. An improvement to this methodology would have been to install 2 PDA's, one on the plant flocculator and one on the inlet to pilot filter – the system dynamic flocculation properties could then have been determined and related directly to filter performance. This could have been carried out over a range of plant conditions to see if meaningful readings could be obtained, and to further understand the factors that contribute to generating a meaningful reading. It was unfortunate that the PDA readings could not be stabilized at the pilot filter inlet as that would have given the most representative measure of the floc size entering the pilot filter column. This was the main reason for using the breakage jar test on the flocculated water, and so that the floc strength and reformation factors could be generated. Useful information confirming the relationship between Fe:DOC ratio and dynamic flocculation properties was obtained nonetheless.

During the trials there were 3 runs that coincided with a lower raw zeta potential which correlated with a more negative flotation zeta potential, and these corresponded to poor filter performance with respect to filtered turbidity and particle counts. During trial 1, and run 3 the flotation zeta potential decreased to -10.7 mV and the filtration performance was noted to be considerably worse during this run compared to the previous 2. The same phenomenon was observed during trial 2 and run 3, except the zeta potential decreased to -12.2 mV. During trial 3, run 3 was effected by the same issue and although the floted zeta potential only decreased to-9.6 mV there was an appreciable deterioration in the filtered baseline turbidity and particle counts. The filter ripening process appeared to be extended in all three cases, comparative to the other control runs during the respective trials. Poorly coagulated particles were thought to be the reason for the comparatively poor filter performance. This presents a strong case for the existence of the lower bound within the operational window for zeta potential of -10m V as found by Sharp *et al.* (2006) to apply to filter performance. The exact range is not known for filtration and is thought to be system specific, but the performance using this system improved as the zeta potential tended towards 0 mV, and deteriorated outside of -10 mV. The cut-off of around -10mV observed in this work has also been proposed in the literature (Logsdon *et al*, 2002).

The dynamic flocculation properties seem to have had less of a contribution to the filter deterioration observed in trial 1 (run 3) and trial 2 (run 3) as there was no significant difference observed in these parameters between trial 1 and trial 2. This suggests that zeta potential was a more influential factor to optimise at the primary coagulation stage with respect to achieving good filter performance, and humic substance removal. This is in line with the findings of Gregory and Carlson, 2003 who proposed that optimization of charge is a more important and robust tool than pH or coagulant dose. The mechanism for this is due to the attachment processes, which are thought to be retarded if zeta potential isn't optimal (McCarthy and Zachara, 1989).

Throughout the trials in Chapter 6 using the DA20 pilot plant, there was a difference observed between the flocculated and floted zeta potential measurements. The tendency was for the zeta potential to decrease between flocculation and flotation, and this effect was accentuated at Fe:DOC ratio of 1.2. In this instance the flocculated zeta potential showed a reversal of charge compared to the raw water from -17 mV around 2 mV, and then after the flotation process the charge reversed to around -4 mV.

This charge reversal wasn't observed in the other trials and is usually thought to be caused by an overdose of coagulant, thereby suggesting that 1.2 Fe:DOC was an over-dose. Previous research by Han and Kim (2000) found that good flotation performance occurred when the bubble and particle were oppositely charged. The flotation performance in terms of turbidity during the final trial at 1.2 Fe:DOC ratio, was the best at <1 NTU, and it's possible that this could be partly due to the effect noted by Han and Kim (2000), if the bubbles were negatively charged. Other researchers have shown that flotation performance is dependent on the ability of the bubbles to adhere to the particles which is a function of the combined zeta potentials of the bubble and particle. Removal efficiency via coagulation has been shown to be related to the product of the bubble and particle zeta potential (Jefferson, 1997). In this work the bubble zeta potential was an unknown element.

The NOM removal was also highest in the final trial so improvements in flotation performance could have been due to improved charge de-stabilisation, which suggests that 1.2 Fe:DOC wasn't an overdose. The flotation process uses water exiting the flotation units (comprising 8% of the flow), which then passed through a packed tower into which compressed air at 5 bar g was drawn. Moorland waters such as Albert WTW raw water are renowned for having a low alkalinity and therefore a poor buffering capability. It is likely that both the air absorption processes occurring in the packed tower, and the flotation process itself had an impact on CO_2 stripping and thereby resulted in decreasing the zeta potential. It would be extremely useful to research this further in order to better understand the mechanism for the decrease in zeta potential, and to predict if the resultant flotation zeta potential would drop below the pre-determined bound of -10mV. This could better inform plant operators how to infer likely filter performance from jar tests if the reduction in zeta potential was consistent in magnitude. This is providing that the observations with respect to zeta potential and filter performance hold true for a wider range of conditions than was studied in this work.

Part 8.2.1 The effect of polymer dose on Albert WTW pre-filtered floc properties and filter performance

Polymeric additives been used in the water industry to alter floc properties since the 1960's. They have generally been used as strengthening agents at the primary coagulation stage or to improve the clarification stage prior to rapid gravity filtration (Bolto, 1995; Bolto *et al*.,1999). It is not conventional to use polymeric flocculants after the DAF process, but it is logical as the DAF process has been shown to cause considerable fragmentation (Leppinen and Dalziel, 2004). It is therefore logical to assume that the floc carried over from the DAF stage to the rapid gravity filters at Albert WTW was partially fragmented, particularly at high plant flow rates and cold temperatures where shear stresses would be highest. Floc fragmentation during the DAF process has been observed by Zhang *et al*. (2009) who carried out a modelling study of the flotation units at Albert WTW and recommended the use of low-energy nozzles that minimize floc shear.

The premise behind the work in Chapter 7 was to use the PDA and the breakage jar test method to identify suitable polymeric additives and doses for optimum re-flocculation of DAF outlet water in the jar test situation, and then to apply the polymer/dose to the pilot filter plant and use the PDA to infer the likely benefits on the dosed floc properties. The PDA was trialled again on the pilot filter inlet but the reading was very noisy and not easy to interpret as seen previously on plant samples. Samples were taken from the pilot plant mixing tank and breakage tests were carried out in order to infer floc characteristics and likely impacts on filtration. It is acknowledged that the mixing tank feed to the filter inlet wasn't accurately hydraulically modelled by the breakage jar test, but the re-flocculation properties could be used to infer likely correlations. The overall concept being tested was whether it was possible to modify floc characteristics just prior to filtration, in order to improve filter performance, and which characteristics had the most impact. The initial set of jar tests carried out on the DAF outlet water over 4 consecutive days showed that three out of four of the polymeric additives exhibited flocculant effects and a good degree of re-flocculation was observed. One of the additives was a cationic polyamine FL17 which was highly charged, and this showed no effect on re-flocculant ability as would be expected given the reasonable degree of colloidal removal already carried out by the flotation outlet stage. The coagulated water was between -5.3 mV and -6.5 mV which were within the optimum range for NOM removal reported in this work, and that of Sharp *et al*, (2004).

Floc Properties and Breakage Mechanisms

The floc in the control systems with no additives exhibited high floc strength factors as well as high floc reformation factors, and also coincided with the smallest floc. This was because the jar test procedure allowed for the re-flocculation of some of the micro-floc carried over from Albert WTW DAF process. The re-flocculation was shown to be completely reversible in the control jar tests with no additives. In these control systems the floc strength was generally higher than the flocculant dosed systems. This result is consistent with what has been observed throughout this work with respect to the negative correlation between floc strength and floc size, and this is also generally reported in the literature. The floc carried over from the DAF has been subjected to considerable shear forces as it passed through the treatment process, and is therefore considerably smaller than its original size. In reality the floc carried over to the RGF stage is likely to be comprised of a mixture of small fragmented floc formed from both surface erosion of the original floc and fragmentation, as a result of the hydrodynamic shear forces encountered within the treatment process. The jar test data from the control systems tends to support this as the flocculation index readings from the jar tests on DAF outlet water were several orders of magnitude smaller than the readings observed in the primary coagulation jar tests presented in Chapter 5 and 6. It is known that the smaller particles in the size range 1-10µm are the most challenging to remove in depth filters (Kim and Tobiason, 2004; O'Melia, 1985; Jegatheesan and Vigneswaran, 2005). It is therefore important to establish suitable means of removal of these particles.

The observation relating to the re-growth of DAF carryover floc without polymer dosing has since been noted by Fabrizi et al., (2010) who has carried out a similar study on the same water source. Their work was based on using 2 types of particle sizers (Mastersizer 2000 and Spectrex PC220) to monitor the effects of dosing AH912 into DAF outlet water on the floc size and strength. The method of measuring floc strength in their study was a jar test based technique as was used in this study. Their results showed that the dosing AH912 enhanced the ability of the DAF flocs to re-grow, with an increase in floc size from 228 to 325 µm. In this work, the actual floc size wasn't measured but the floc index derived from the PDA is representative of floc size. In this work the flocculant dosed floc was larger, and generally the dose was proportional to FI_{max} and $FI_{ref.}$ In this work the larger floc was noted to be weaker and less reversible, but in the work of Fabrizi *et al.* (2010); the larger floc was shown to be stronger and more reversible.

The reason for this difference could have been due to differing velocity and shear profiles between the two tests in combination with the different measurement techniques and their sensitivities. In their work it was noted that the polymer dosed floc started re-growth during the breakage period which wasn't observed in this work. In this work the breakage period was relatively brief (30 secs) as compared to 15 min in the study by Fabrizi *et al*. (2010). In reality the actual breakage period experienced by floc onsite between the DAF outlet and the filter inlet varied depending on the filter inlet relative to the location in the channel. A more informative test would be to model the flow into the filters and determine the actual residence time in the system alongside estimates of the shear forces and adapt the jar test accordingly. This could be done either by physical scale models or CFD analysis.

In order to explore this further, the role of the flocculants used needs to be understood and the literature is fairly extensive in this regard. The mechanism for re-flocculation following addition of non-ionic and weakly charged polymers as used in this study is well understood (Muhle and Domasch, 1990). The polymer molecule adsorbs to the particle whilst the remaining part of the macromolecule extends into the bulk solution whereupon it bonds to other particles in suspension and inter-particle molecular bridges are formed (Bolto and Gregory, 2007). This explains the mechanism by which the flocculant dosed systems re-aggregated.

The reason for the linearity between the polymer dose, FI_{max} and FI_{ref} was likely to be as a result of increased bridging potential as the dose increased which resulted in larger floc. The difference in reversibility between this work and that of Fabrizi *et al*. (2010) is not known but is thought to be due the differing measurement techniques and accuracies or different regime. The PDA derived flocculation curves used in this work had to be "smoothed" by use of the moving average function which may have added an inaccuracy factor into derivations of the floc strength factor and floc reformation factor. It is possible that by removing some of the data spikes to enable graphical analysis, an error was added. However the interpretation of the flocculation curves before the "smoothing" process would have been equally erroneous. It is likely that the DAF outlet water contained a variety of particles within a reasonably large size distribution, and some of the larger particles may have skewed the flocculation index data and so it was correct to remove those from the curves. There are two possible mechanisms by which the non-polymer dosed system re-aggregated:

- Adsorbed NOM acting as a bridging component (Walker and Bob, 2001)
- Charge neutralization mechanisms and Van der Waal's forces given that zeta potential conditions were favourable for attraction (Chaignon *et al*., 2002)

In reality both mechanisms were likely to be operating in tandem, but with the second mechanism more influential given that NOM lies relatively flat to the particle it is adsorbed onto and therefore bridging would most likely be minimal. Overall the initial polymer dosed jar tests showed that the three flocculants increased the floc size above that of the control systems, and improved the settled turbidity. The results did not show overall that the floc strength or reformation was significantly improved in all of the flocculant dosed systems compared to the control systems. The difference in size between the dosed systems and the control systems is important and could be fundamental to explaining the decreased floc strength factors observed in the dosed systems.

If the control systems generated floc that was generally smaller than the microscale of turbulence, then it is logical to say that the breakage mode would have been surface erosion from the parent floc. In this case less of a reduction in size could be expected and this explains the higher floc strength factors observed in the control systems. Conversely in the polymer dosed systems, the floc size was larger at the breakage stage and consequently may have been larger than the microscale of turbulence. In this case, considering also the lower floc strength factors observed the breakage mechanism of fragmentation is more likely in the polymer dosed systems. The conclusion of Fabrizi *et al*. (2010) was that the polymer dosing reduced the release of erosion particles from the floc as judged by a decrease in the concentration of small particles, and an overall increase in the larger particle sizes. The discrepancy between the two conclusions was thought to be due to differences in the measurement techniques and inherent sensitivities and accuracies as described earlier. The general observations made in both studies with respect to the increase in floc size as polymer dose increased were in agreement. Pilot filtration trials were carried out alongside breakage jar tests using water from the pilot plant mixing tank which contained the DAF water dosed with the flocculants AH912 and AN905. The experimental time remaining allowed for the investigation of two flocculants, and given the three flocculants exhibited similar dynamic flocculation performance, the decision to use AH912 and AN905 was based on settled turbidity.

The concept of taking the water from the mixing tank above the pilot filter was similar to the concept of taking the water from DA20 flocculator inlet as seen in Chapter 6. Any difference in the initial mixing conditions in the jar test compared to the pilot plant mixing tank was therefore eliminated by flocculating the sample taken from the mixing tank. It is acknowledged that the hydrodynamic conditions within the jar would have been different to the mixing tank and the filter inlet arrangement as the geometries were not the same, and therefore there would complexities to explain when attempting to relate the floc properties measured in the jar test and the filter performance.

Albert WTW DAF outlet water quality was slightly different between the initial jar tests and the pilot filter trials and the polymer dose range was revised accordingly as the original dose range didn't result in appreciable re-flocculation. The pilot plant feed water was also moved from to upstream of the lime dosing due to numerous breakdowns on the plant which may have disrupted the pilot plant work. The pH change was not found to alter the polymer interactions with the floc, as seen by comparisons of the settled turbidity of DAF water dosed with AN905 at both pH 4.5 and pH 6.5. The relationships between FI_{max} and floc strength factor seen throughout this work were also found to be true when using AH912. The set of flocculation curves generated using AN905 in the second polymer dose trial were too noisy to interpret as previously and so no dynamic flocculation parameters were generated from these graphs. The reason for the "noisy" graphs during the second polymer trial was thought to be due to the lower floted water turbidity (<3 .5 NTU as compared to >4 NTU). This may have been due to a lower concentration of particles of a smaller size carried over from the DAF units but this wasn't measured. A particle counter was installed on the DAF outlet for a short period of time but considerable fouling formed in the measuring cell and it was therefore discontinued. It was also thought that due to the high numbers of particles (>1000/ml), obscuration would have been an issue and the trends may not have been useful.

The flocculation curves generated from the pilot plant mixing tank using AH912 showed complete reversibility of the floc, and in most cases the floc reformed to a greater extent after the breakage period. This effect was noted by Fabrizi *et al*. (2010) but wasn't apparent in the previous set of jar tests. The flocculation index at the start of the initial jar tests using AH912 was approximately half the magnitude of the values at the start of the pilot mixing tank jar tests.

This could have been due to the fact that residence time in the pilot plant mixing tank would not have been the same for all floc, and it is likely that some floc within the system had already re-flocculated to some extent by virtue of being in the tank longer. This could have impacted on the reformation factors observed and provides an explanation for the increase in reversibility. The relationships between the polymer dose, FI_{max}, FI_{ref}, floc strength factor and floc reformation factor all showed the same trends as seen in the initial polymer jar tests.

The zeta potential of the water entering the pilot filter column was stable between the two polymers used, and also over the concentration range applied. The zeta potential decreased slightly at the highest dose of AN905 as would be expected given the mild anionic charge, but the decrease was not considered to be significant. Organics removal was noted to increase in terms of UV_{254} absorbance removal and DOC removal between the flotation outlet and filtration outlet. The magnitude of the removal was most significant at a dose of 0.05 mg/l of either polymer. There was a difference in sensitivity between the two methods of measuring the organic removal, with the UV_{254} absorbance method showing the greatest sensitivity to the polymer dose changes. This has been observed before by Kerry *et al*. (2002). Their study showed that UV_{254} absorbance removal was substantially higher than DOC removal for waters coagulated with Alum. The implication was that the coagulation process was selectively removing a greater portion of UV-absorbing compounds than bulk DOC. In this work, it is probable that the flocculants targeted a particular component of NOM which was UV-absorbing but not necessarily a large component of the bulk DOC. This would be very interesting to research further by use of HPSEC to understand the types of compounds within the residual NOM which may have been selectively removed by the use of the flocculants.

The filter performance during the control runs (no data included due to corrupt disk), and at the lower doses of polymer (up to 0.02 mg/l) was very poor in terms of effluent particle counts and turbidity. Filter breakthrough was observed to occur within 10-15 mins (40 litres) during the control runs, and the breakthrough was extensive. At the lowest doses of 0.005 mg/l and 0.01 mg/l the baseline filtrate quality was very poor and the duration of the baseline period was short. At Albert WTW at the time of this work, the trigger to backwash the RGF filters was set to 0.5 NTU based upon a risk assessment related to cryptosporidium breakthrough. If this had been applied to the pilot filter, the filter runs would have been extremely short and in some cases <2 hours.

It is apparent that the inlet water quality and conditions were not conducive to good filter performance. A likely reason for the extremely poor performance was that the zeta potential of the floted water outside of the operational window according to Sharp *et al*. (2006) of -10mV to +3 mV. The floted water UV_{254} absorbance measurements were high (7-8 abs/m) and outside of the full-scale plant operating trigger (<5 abs/m) set to minimize THM formation. The implications were therefore that the coagulation conditions were not optimal during the trial using AH912 and as a result the filter performance was sub-optimal.

The filter performance in terms of filtrate quality improved substantially as the polymer dose increased. The filter run time before the onset of breakthrough increased substantially as the dose increased, and at the highest dose of 0.05 mg/l the breakthrough was eliminated. The filter performance was extremely poor during the control runs, which was attributed to the poor coagulation performance as measured by high zeta potential/UV_{254} absorbance, but the performance was substantially improved after polymer addition. This implies that the poor charge destabilization was overcome by the effect of the polymer addition. The initial jar tests and the mixing tank jar tests both the indicated that the relationship between polymer dose and floc size was linear. It is likely that the floc entering the pilot filter column increased in size as the polymer dose increased. The effects observed on the pilot filter performance in terms of increased run time within operating parameters, and improved baseline filtrate quality were therefore most likely to be due to increase in floc size. The final run using either polymer at 0.05 mg/l was characterized by a lower UV_{254} absorbance (3 abs/m) but with no change in zeta potential or DOC. The filtrate quality was very good at this dose and no breakthrough occurred. The flocculation index readings at the start of the mixing tank jar tests were indicative of the floc size within the mixing tank. These indicated that the floc in the mixing tank was considerably larger during the final trial at a dose of 0.05 mg/l of either polymer. The removal of UV absorbing compounds over the pilot plant was also significantly higher at the dose of 0.05 mg/l.

The data from the trial using AH912 and AN905 indicated that the reason for improved filter performance was mainly due to the likelihood of increased floc size formed from the interaction of the flocculants with the floc carried over from the DAF units. The removal of UV absorbing compounds over the pilot plant was also significantly higher at 0.05 mg/l polymer dose, suggesting some degree of flocculant/residual NOM interaction. This may have been a contributory factor in the much improved filter run without breakthrough achieved at this dose, but it is difficult to separate the two influences of floc size and chemical nature. Zeta potential was not a contributory factor in the improved filter performance as there was no difference between the runs. The filter breakthrough observed in the control runs and at the lower doses of polymer could be related to poor attachment processes, which could either be poor floc-grain collector efficiency or poor floc-deposit collector efficiency.

Some of the behaviour observed in this work can be related to the previous studies by Bache and Gregory, (2007) whom suggested that floc size and strength were intricately related to filter performance. They showed that filter headloss development rate was lowest when the Camp number was highest. In terms of floc size the highest Camp numbers generated the smallest floc due to the relationship between floc strength and size – smaller floc being stronger. This meant that the headloss development rate was directly related to floc size, with smaller floc resulting in lower headlosses. In this work, the headloss development rate was also found to relate directly to the polymer dose which was inferred to relate to floc size going onto the filter. In the work of Bache and Gregory, (2007) they identified that the following factors are important to the filtration process:

(i) floc water content appears to affect the loading rate;
(ii) floc sizes must be sufficiently large to permit transfer to a collection surface;
(iii) flocs must be suitably conditioned to enable capture (normally achieved by effective coagulation);
(iv) the ‘bigger is better’ approach is not necessarily appropriate in situations in which floc/deposit strength plays a controlling role in the removal process.

In this work there was more than one variable due to the nature of the raw water system being studied. What can be said from this work is that the filter performance during the control runs was extremely poor and this was most likely to be due to a combination of poorly charge-neutralised floc and floc size. The weighting of each factor was not known exactly but it was evident that the polymer dose, especially at the higher doses increased the run time before breakthrough without altering the charge. The impacts of floc size are therefore considered to have a high weighting out of the above factors in the improvements in the pilot filter filtrate quality that were achieved by the addition of the two flocculants.

The impact of the floc/deposit strength was tested by means of performing a flow-change onto the filter – two runs were subjected to a 50% flow-change after 3 hours and two runs were subjected to a 50% flow-change after 6 hours. The flocculant tested in the flow-change experiments was AH912 at 0.05 mg/l. The results for the flow-changes at 3 hours were interesting in that they showed no breakthrough during the run. Researchers such as Cleasby *et al.* (1963) reported that increases of <30% had no impact on breakthrough on full scale plants, providing filters were not already clogged. Researchers such as Thurston *et al.* (2000) indicated that 50% flow changes caused breakthrough when using aluminium based coagulants at cold temperatures. The flow changes imparted during this work were therefore considered to be high enough to "shock" the filter bed, especially as temperatures were colder than those described by Thurston *et al*. (2000). In the control runs with no flocculants, breakthrough was significant (partly due to the poorly optimised coagulation conditions). The flow changes at 3 hours in this work didn't result in breakthrough as measured by particle counts or turbidity. The exact reasons for this are complex, but using the knowledge gained from both sets of jar tests the lack of breakthrough can be explained further.

The jar tests all pointed to the main effect of dosing the flocculant into the mixing tank, was an increase in floc size entering the pilot filter column. The breakage jar test showed that as polymer dose increased the floc size increased, and floc strength factor decreased. The filter performance also improved substantially as the polymer dose was increased to 0.05 mg/l.

The improvement in filter performance of the poorly charge neutralized water was deemed to be mostly due to the increase in floc size. The filter was subjected to a 50% flow change after 3 hours on similarly poor charge neutralized water (zeta potential >+3 mV) dosed with 0.05 mg/l AH912 and no breakthrough occurred. This implies that the magnitude of the increase in hydraulic shear forces caused by increasing the flow by 50% was less than the strength of the floc deposit.

This could mean that the floc already deposited within the pores remained where it was during the period of increased shear, or was detached from the media grains and then reattached further down the bed. Another mechanism is that proposed by Jung *et al.* (1996) who suggested that at low shear rates, flocs restructure rather than break up or detach. As the flow change occurred after the ripening phase, it is assumed that there was a good deposit of floc already on the media grains acting as collectors. It was not possible to tell the origin of the floc in the filtrate, and so the exact mechanisms of floc detachment/attachment occurring within the bed during flow changes were unknown. This would be an important area to research further to identify what properties of flocs are most important to ensure filtrate quality is maintained throughout flow changes, as flow changes are a normal part of filter operation.

The second set of flow change experiments carried out at 6 hours into the run and with the same magnitude (50%) flow increase, showed that breakthrough did occur on both occasions but was delayed until approximately 6 hours after the flow change. Research by Fitzpatrick *et al*. (1999) on the particle shedding effects due to flow changes in the latter stages of the filter run, found that particles can shed considerably at this stage with only a small magnitude flow change, partially due to the media having collected more particles than in the early stages in the run. In this work, the breakthrough didn't coincide in time with the flow change but occurred much later on in the run. This implies that at the time of the flow change the media wasn't particularly clogged with deposit. This means that the interstitial velocities were not high enough to shear the floc from the media at the time of the flow change. As the run progressed the bed was more clogged and interstitial velocities increased whereupon the shear forces reached a point where they were greater than the deposit attachment forces, and breakthrough occurred. The control runs without polymer dosing had already shown extensive breakthrough after 1 hour of filtration, and at the time of the flow change in these runs the magnitude of particle counts and turbidity increased considerably.

The results of the pilot filtration trials indicated that a small dose of the flocculant polymer AH912 improved the pilot filter performance by limiting breakthrough and improving resilience to flow changes. At the end of this work, the pilot plant trials were scaled up and 0.05 mg/l of AH912 was dosed into Albert WTW filter inlet channel through means of a sparge pipe an carrier water. The full scale plant trial and results fell outside of the remit of this work, but the Yorkshire Water report has been included in the appendix for completeness. The report findings were generally consistent with the pilot plant experiments with respect to the polymer dosed filter runs showing reduced filter breakthrough, and longer run times within acceptable water quality parameters.

Part 8.3 The use of the PDA and the breakage jar test technique to derive floc properties – advantages and disadvantages

One of the novel aspects of this work was the use of the PDA to monitor the coagulation performance of the natural raw water systems with different coagulants, which hasn't been done extensively before. The majority of the studies prior to this work have been on kaolin based systems, which are more ideal than realistic. This work also used the PDA to monitor the re-aggregation of partially treated water. In this regard the PDA flocculation index reading was found to be too noisy to interpret at low turbidities (<3.5 NTU), which has since been noted by Gregory, (2009). This is a limitation of the PDA as at low concentrations of particles the output is subject to random electronic noise which renders the reading unusable. This was the main reason that the PDA was not used on the DA20 plant or Albert WTW to measure the flocculation index at the flocculation stage and the flotation outlet stage in order to measure the system floc strength, as the turbidity was not high enough at the times it was tried. The turbidity on the main plant flotation outlet could easily be >3.5 NTU at some points, so the concept of using the PDA as an online monitoring tool is worth testing further as discussed in Chapter 9.

The other limitation encountered in this work in Chapter 5 was the flocculation index readings at pH 6.5 which were smaller than they should have been. It was quite apparent visually that the floc formed at pH 6.5 was much larger than at pH 3.5 and 4.5 but the flocculation index readings were not representative. This has since been shown by Yu *et al*. (2010) to be due to hydroxide flocs having a scattering cross section much greater than their projected area. This prevents the PDA from providing accurate representations of the floc size, strength factor and reformation factor under "sweep" flocculation conditions.

The breakage jar test was used in combination with the PDA to derive the floc strength factor by calculation of the ratio of the flocculation index after breakage to the maximum flocculation index. Essentially the technique used falls into the category of macroscopic floc strength tests where the system is exposed to a level of increased shear and the floc size before and after breakage is used to quantify the strength factor. This is different in essence to the absolute floc strength as the floc was formed which is related to the hydrodynamic shear conditions, and the floc strength factor. There are some researchers who refer to stronger floc as larger floc (Bache and Papavasilopoulos (2003), Gregory and Yukselen (2004)). It is generally agreed that floc size is a dynamic equilibrium between floc break-up and aggregation. The researchers who refer to the larger floc being stronger floc are basing their interpretation on the model proposed by Biggs and Lant, (2000) who showed that floc size is a balance between floc growth and breakage. This implies that larger flocs are therefore able to resist breakage, in order to reach their large size. This is then confused by what happens to flocs when they are exposed to increased shear. In this case it is generally accepted that larger flocs break down more extensively and therefore have lower floc strength factors (Jarvis *et al*. 2005). The effect of different shear regimes on floc size and strength is currently not well researched and would provide useful information with regard to the energy dissipation rate, floc size, strength and breakage mode. Floc strength factor gives an idea of how the floc will behave under shear, and relative comparisons under the same shear regime can give an idea of the mode of breakage. The results generated in this work were generally consistent with the model of larger floc exhibiting lower floc strength factors, although there was one exception in Chapter 5 at pH 4.5 whereby the floc size increased with Fe:DOC but showed no decrease in floc strength factor. A further limitation of the PDA and the method used in this work is noted when it comes to defining the breakage mode. It is thought that the floc size relative to the eddy size is of importance and relates to which breakage mode the floc will undergo (Thomas *et al*. 1999).

The PDA can't produce an absolute floc size and the energy dissipation rates were not quantified in this study, therefore the floc size relative to the eddy size wasn't known. Analysis of the breakage modes was therefore more subjective than if the absolute floc size was known in concert with the energy dissipation rate. The main advantage of using the PDA to monitor the flocculation process is that it is a semi-empirical technique that is superior to the jar test alone. The difficulty lies with interpreting the results and relating to plant performance and the wider literature, in light of the disadvantages mentioned above. This issue is not unique to the PDA and most other floc strength measurement techniques are subject to similar issues with respect to comparison and normalisation with other techniques.

Chapter 9 Conclusions and Recommendations

This project has expanded on previous studies using Albert WTW raw water and the Mastersizer 2000 by using an alternative means of studying floc properties using the PDA and the breakage jar test technique. This project has also extended this field of study to include assessment of how parameters such as surface charge and floc properties are inter-related and may impact on filter effluent quality. The method used in this project to quantify the floc properties such as size, strength factor and reformation factor was a modified jar test procedure using the PDA. This method involved measuring the flocculation index before and after a period of applied shear, and the main conclusions relating to determination of boundary conditions for using the PDA are as follows:

- Flocculation index was not representative of the floc size when operating under "sweep" flocculation conditions at coagulation pH 6.5.
- The flocculation index of the flotation outlet water was not representative of the floc size when the turbidity was < 3.5 NTU, and the reading was too noisy to interpret.

Both of the above limit the use of the PDA for application as a tool for studying floc properties when operating outside of normal operation. Normal operation is used in this context to mean primary coagulation by charge neutralisation, which is not dominated by the hydroxide sols reputed to control the "sweep" flocculation process. When using the PDA within the normal operational envelope the conclusions relating to its suitability for floc monitoring humic floc are as follows:

- Flocculation index data was consistent under the equivalent controlled conditions, therefore the technique was reliable.

This work did not attempt to quantify the actual floc size and correlate with the flocculation index, and so it can't be said that the flocculation index data was directly related to floc size.

Raw and DA20 flocculated water used in the jar tests presented in Chapter 4 to 6 was mostly of a similar character as quantified by a raw water SUVA value within a similar range of representative compounds. The following can be concluded, with respect to the impact of the coagulant matrix on floc properties and NOM removal:

- Floc formed with polyDADMAC and the dual coagulant systems of ferric sulphate and Zetag 64, and ferric sulphate and polyDADMAC grew to a larger size during the initial growth phase, and the re-growth phase compared to ferric sulphate; but was less resistant to breakage compared to ferric sulphate due to its larger size.
- NOM removal was highest using ferric sulphate, and only slightly lower using the dual coagulant systems, but was significantly lower using the polymeric additives on their own.
- FI_{max} was found to be related to coagulant dose, R_{FI} and NOM removal for the single coagulant systems where charge neutralisation or patchwork agglomeration was the coagulation mode but when the NOM removal mode was a mixture of charge neutralisation and polymer-bridging (as was the case in the combined coagulant systems) there was no correlation between R_{FI}, dose or NOM removal.
- In most cases the impact of increasing Fe:DOC generally related to increased FI_{max}, and as a consequence of the floc being larger it was less resistant to the high shear period than the smaller floc formed at the lower ratios, and the floc strength factor decreased. There was an exception at coagulation pH 4.5 and Fe:DOC 1.4-2 where floc size increased but strength factor remained the same.
- NOM removal was comparable between pH 4.5 and 6.5 but due to the under-reading of the PDA at pH 6.5 it is not possible to conclude whether there were any differences in floc properties formed at pH 6.5 compared to pH 3.5 and pH 4.5. NOM removal was poor at pH 3.5 at around 50% but the "patchwork agglomeration" floc formed at this condition was considerably larger than at pH 4.5, and showed greater reformation factors. Increases in Fe:DOC had no impact on NOM removal or surface charge at this condition but did correspond with R_{FI} and FI_{max}.

- At coagulation pH 4.5 and Fe:DOC 0.7-1.2 there was generally a positive correlation between Fe:DOC ratio, FI_{max} and zeta potential; and good NOM removal performance coincided with a zeta potential tending towards 0 mV. Overall analysis revealed that both zeta potential and FI_{max} were correlated with each other, and the Fe:DOC ratio; but there was no significant correlation found between floc properties and NOM removal. This implies that Fe:DOC has the most bearing on the floc size when the dose/zeta potential are within the range for good NOM removal.
- Zeta potential was shown to correlate with good NOM removal within an operational window, and the upper end of the window was found to correspond to approximately 3 mV but the lower end was more difficult to determine.
- Filter performance in terms of filtered water quality was assessed at coagulation pH 4.5 using a range of Fe:DOC from 0.7-1.2. In this case the most significant correlations were found between zeta potential, FI_{max} and outlet water quality. Filtered water quality was seen to improve as the zeta potential tended towards 0 mV, with notable deterioration in the form of breakthrough observed at <-10 mV. The correlation between FI_{max} and filtered water quality may not have been valid as FI_{max} was measured in a jar test using flocculated water and not on the pilot plant filter inlet – and may therefore not be indicative of the true size of the floc entering the filter although it could be related. This means that the relative impact of floc size on the filter performance could not be established.

Taken overall the results of this work support the concept that floc properties as measured by the PDA can lend extra weight to deciding the optimum coagulation conditions, but it is not recommended to use PDA data such as R_{FI} and FI_{max} in isolation of NOM removal or surface charge data. Overall the data implies that in terms of NOM removal; systems that produce larger floc are superior to ones that produce smaller floc, and this is despite the decreased floc strength factor observed with increased floc size. Floc reformation factor was not found to be significantly correlated to any of the measured parameters at coagulation pH 4.5. The inverse correlation of floc strength factor with FI_{max}, which generally correlated well with NOM removal indicates that it is not a useful parameter to consider when optimising for NOM removal.

The final set of experiments in this project focussed on the use of flocculants to condition floc just prior to filtration during challenging winter conditions when the water temperature was 7 °C; and the filters at Albert WTW were experiencing the phenomenon of premature filtered turbidity breakthrough at low headloss. The PDA was again used in an application outside of its normal operating regime, and the following was concluded from the pilot-scale filter experiments and jar tests:

- Flotation outlet water during these tests was positively charged with a zeta potential of around 4 mV, and the pilot filter outlet quality with no additives was extremely poor and breakthrough occurred within the first 1-2 hours of the filter run.
- The addition of the flocculants to flotation outlet water generally had no impact on surface charge and they were observed to act by bridging micro-floc together to form larger floc, and the size of the resultant floc was proportional to the applied dose.
- When applied to the filter influent water, the same general trends as above were observed using the flocculants AN905 and AH912; and as the dose increased, the filter headloss development rate increased proportionally. Filter effluent quality improved significantly as the dose increased, and filter run time before breakthrough was extended considerably. The same trends of increased FI_{max} and decreased floc strength factor were noted in this case, but reformation was generally >100%.

Taken together these results suggest that conditions of sub-optimal charge neutralisation as typified by a zeta potential outside of the operational window; can cause poor filter performance in the form of very early turbidity and particle count breakthrough. This can be recovered by the addition of small doses of flocculants prior to the filter unit and good quality filtrate can be produced. Furthermore the flocculant dosed filter can withstand the hydraulic shock imparted by 50% flow changes at 3 hours and 6 hours into its run without particle shedding into the effluent. The results from the flocculant dosed filter experiments were used to inform and implement a full-scale plant dosing scheme. This was carried out at the end of this project and the results from a Yorkshire Water report (included in the appendix) on the scheme found it to be beneficial for increasing filter run time, reducing breakthrough and increasing plant output by approximately 5-7 Ml/d.

Part 9.3 Recommendations for Further Research

Part 9.3.0 The PDA as an online monitoring device

Part of this work involved some preliminary testing to assess the potential to use the PDA as an online analyser, which on the three occasions that it was trialled proved difficult as the reading was difficult to interpret at the pre-filtration stage presumably due to low particle concentrations. There is the potential to continue with the initial trials, to extend the range of conditions experienced onsite and further assess the PDA in this regard. The instrument could be installed onsite and the feeds could be alternated between the different stages of the treatment process to assess the flocculation index as the floc passes through the process. The readings of flocculation index could then be used to calculate the system floc strength, and to gain some appreciation of floc size and how it changes through the process. A fuller understanding of the impacts of temperature, coagulation performance and plant flow on floc strength, breakage and subsequent filter performance could then be obtained.

This would ultimately be a superior method to the breakage jar test used in this work, as the floc shear regime would be equivalent to the actual main plant conditions. The comparison of the two flocculation index readings would therefore be more representative of the floc on the main plant as the hydrodynamic shear forces would be equivalent. In this way the impacts of floc size and strength on filter performance could be studied further. The initial trials carried out in this work were not extensive and found that the online reading from the filter inlet was difficult to interpret below a turbidity of around 3.5 NTU. A longer trial period is recommended. The PDA lends itself to this type of application as it is fundamentally very portable and easy to install onsite, but if further work in this regard proves too erroneous at low turbidity as initially found in this work, other instruments such as the Mastersizer could be used instead although they are less portable.

Part 9.3.1 Further pilot plant studies

The pilot plant trials involving the DA20 in this work were cut short due to equipment resourcing and break-downs, but it would be very useful to continue in the study of combined coagulant performance which gave some interesting jar test results in Chapter 4 of this work. In this way combinations of ferric sulphate and small quantities of flocculant polymers added at the primary coagulant stage could be investigated to find the optimum for improved floc properties, NOM removal, and filter performance. It would be particularly useful to study this during challenging conditions on the plant such as low temperatures and changeable raw water quality. The PDA could also be optimised for online monitoring of the flocculation index at the coagulation stage, flotation stage and then pre-filtration stage to assess the system floc strength, and extent of breakage and reformation due to the shear stresses within the treatment process. This could be trialled to test conditions both within and outside of the operational window of zeta potential. In this work, the zeta potential was found to change significantly between the flocculation stage and flotation outlet, and it would be useful to gain more data on this and understand the mechanisms, whether the change is due to air-stripping of the poorly buffered water or whether the DAF bubbles were imparting an effect. This could be carried out by analysing zeta potential changes from flocculation to flotation on WTW with differing alkalinity to determine the impact of the buffering capacity of the water on the zeta potential.

The pilot filtration studies using the flocculant polymers AH912 and AN905 could also be extended to include online monitoring of the flocculation index before polymer addition, and then at the filtration inlet stage. If the PDA reading was not representative then alternative sizing techniques such as the Mastersizer or particle counting could be explored. In this way the impact of the flocculant dose on the floc size presented to the filter would be known. The headloss could be measured throughout the filter bed in order to determine the floc size that causes surface clogging rather than depth filtration, and the polymer dose could be optimised accordingly. This would be beneficial as the main plant has installed a polymer dosing system prior to the filtration units, and knowledge of the impacts of the polymer dose on the headloss is vital for good long-term filter operation. Over-dosing of flocculants should be avoided as this can lead to formation of filter "mudballs" which can reduce the filter performance and lead to considerable downtime as the media would have to be removed.

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Appendix

Appendix 1

The DA20 pilot plant comprised of a submersible pump placed into Albert WTW raw water feed chamber, this fed the DA20 plant via a 6 inch flexible hose. The water flow was metered on the inlet to the pilot plant so that the volumetric throughput could be maintained at the same level. The upper limit of flowrate through the DA20 pilot plant was $20m^3$/hr, so the experiments were designed to run at $15m^3$/hr to be well within the design range. The effluent water could either feed back into the impounding reservoir or feed the pilot filtration rig depending on the position of the outlet valve. The following procedure was followed in order to run the DA20 pilot plant experiments:

1. Open DA20 plant inlet butterfly valve fully
2. Turn on submersible raw water feed pump
3. Open DA20 plant outlet valve so that effluent water is fed to pilot filter plant header tank. Valve between pilot filter plant header tank and mixing tank is shut initially.
4. Adjust DA20 plant inlet butterfly valve to obtain the correct flow reading on the inlet flow meter
5. Adjust flowrate through air absorber to achieve the correct recycle flow
6. Monitor plant until raw water pH readings are stable
7. Open Ferripol XL feed line
8. Start Ferripol dosing pump and set to required flowrate. Check flowrate by drop test.
9. Leave plant to settle for 30 minutes. Check that pH reading has stabilised.
10. Open Kalik feed valve and start up dosing pump. Set dosing pump up manually to achieve desired coagulation pH.
11. Leave pilot plant for 30 minutes to establish stable conditions as measured by consistent pH and effluent turbidity readings from online monitors.
12. Monitor UV_{254} absorbance readings throughout the DA20 pilot plant to ensure consistency and once the outlet turbidity is stabilised and there is consistency in UV_{254} absorbance readings then the header tank outlet valve can be opened on the pilot filter rig and flow can proceed into the pilot filter mixing tank.
13. Data-logging equipment should be turned on and recording started by pressing “play” on the pico-log software interface. This should start all online recordings as all online monitors connected to the Pico-Log software and laptop via RS232 cable. Particle counter should be turned on and WQS Vista software set to record.
14. Open pilot filter mixing tank outlet valve
15. Open pilot filter outlet valve approximately 1.5 turns until flowrate reads 1.5 l/min on the rotameter and the MagFlow flowmeter.
16. When filter run finished the following procedure was followed.
17. Pilot filter outlet valve closed.
18. Header tank and mixing tank outlet valve closed.

19. DA20 pilot plant feed to pilot rig closed.
20. Ferripol XL and Kalik dosing pumps turned off and feed valves closed.
21. DA20 feed submersible pump turned off
22. DA20 plant electrically isolated.
23. Pilot Filter backwash outlet valve opened.
24. Air scour inlet valve opened and flowrate set to 12.5 l/min for 4 mins.
25. Backwash inlet water rotameter opened and flowrate set to 2 l/min for 4 mins
26. Air scour inlet valve closed and backwash inlet water rotameter adjusted to 6l/min for 8 mins
27. Rest period of 5 mins

Appendix 2

Solid Flocculant Make-up Procedure

The manufacturer's guidelines were followed for the make-up of the bulk flocculant solutions that were used in the jar tests. These were as follows:

1. Weigh out required amount of flocculant
2. Transfer flocculant powder to volumetric flask
3. Add a couple of drops of iso-propyl alcohol (wetting agent)
4. Make-up to required volume with de-ionised water
5. Put suspension on a magnetic stirrer for 3 hours
6. Discard solution after 1 month